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Quantitative Experiments in General Chemistry

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QUANTITATIVE EXPERIMENTS

QUANTITATIVE EXPERIMENTS IN GENERAL CHEMISTRY

BY

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PREFACE

The simple quantitative experiments which have hitherto been published as illustrations of chemical laws and theories include so little of the material which appeared available, that it was thought worth while to examine somewhat thoroughly the many reactions which seemed promising for this purpose. The results of this examination are given in this little book. All the methods and experimental details have been subjected to careful laboratory criticism, and an effort has been made to reduce the necessary apparatus and manipulation to the lowest terms consistent with fairly accurate results. A few of the experiments which have become familiar in laboratory manuals have been omitted, as giving too uncertain results, or as too intricate in their performance, and most of those which have been retained have been more or less modified, and, it is hoped, improved.

The quantitative character of chemistry needs to be impressed on the student; while a few experiments of a quantitative nature are usually included in the first year's laboratory practice, most of the quantitative work offered to undergraduates consists of refined and time-consuming determinations, which teach manipulation, but not much chemistry. These methods must be mastered by those who intend to make chemistry their profession; but a course which should emphasize the quantitative relations by means of a comparatively large number of determinations, simple enough to be readily and rapidly performed, is

likely to be of more educational value to students who do not expect to become chemists. The discussion of a wide variety of actual laboratory results would bring home to them the real meaning of the fundamental laws they have studied, and give them a clearer comprehension of the connection between facts and theories.

This collection of experiments may serve as a laboratory guide for such a course, and also furnish suggestions for the enrichment of the first year's work.

While many of the methods which are described are of a comparatively rough character from the standpoint of the exact analyst, the results, in many instances, may be quite as good as those often obtained by the student in carrying out the more elaborate procedure which is usually prescribed. Some indication of the degree of accuracy which may be expected is given in examples from actual experiments.

J. T. S.

October, 1908.

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QUANTITATIVE EXPERIMENTS

I

GENERAL DIRECTIONS

Weighing. None of the substances used for the experiments should be placed directly on the balance pan, except compact pieces of metals; other solids, usually in the form of powders, are put on a previously weighed watch-glass or in the crucible or tube in which the reaction is to occur. When the substance is weighed on a watch-glass, it is transferred to the crucible or tube by means of a piece of glazed paper, a small stemless funnel and a camel's-hair brush.

All objects should be dry and at room temperature when weighed. Crucibles and tubes in which substances are to be weighed are cleaned, heated above 100°, and allowed to cool before they are placed on the balance. Powdered substances are freed from moisture by heating for a time to a temperature above 100°, or, if they decompose at such heat, by standing over concentrated sulphuric acid in a desiccator. After drying, the substance should be kept in a desiccator or in a stoppered tube or bottle.

The beam of the balance is supported when not in use, to avoid unnecessary wear of the knife-edges. When it is released for weighing, the movement should be slow and steady to prevent injury. The beam should always be arrested before making any

change in the load on either pan. The pans should not be allowed to swing sideways while weighing.

Weighings are made with the balance swinging; if on releasing the beam it does not swing, it is started by fanning one of the pans with the hand, or arresting and releasing it again. The index should make excursions through a distance of six or eight scale divisions. After one or two swingings, the turning points of the index are noted, and the point on the scale midway between them is taken as the point of equilibrium.

Before each weighing or consecutive series of weighings, the point of equilibrium or "zero point" of the empty balance is determined, as this is likely to change from time to time. If the zero point is found to be more than one scale division from the middle mark of the scale, the balance should be adjusted by means of the nut at the end of the beam. In weighing an object, the weights are changed till the index swings symmetrically about the zero point. The weights should always be handled with forceps reserved for this purpose, and added and removed in a systematic order. The object to be weighed is placed in the left pan and the weights in the right, the larger ones in the middle of the pan.

When the weighing is completed, the weights on the pan are noted and their sum recorded; this record is then checked by reading the weights again as they are removed and replaced in the box. This precaution should always be taken, as otherwise mistakes are apt to occur. Careful records of all weighings should be so kept that no confusion can arise.

It is usually better not to attempt to weigh a definite amount of a substance, such as 1.000 or 1.500

grams, but to weigh, as exactly as possible, about the quantity required.

Objects which can not be balanced on the pan are hung from the hook over the pan by a loop of fine wire.

Fitting up Apparatus. *Soft glass tubes* for connections are bent to any desired angle by heating in the flat flame of an ordinary illuminating burner. The tube is slowly turned in the flame until the glass yields easily, then removed from the flame and bent. *The hard glass tubes* used in many of the experiments are drawn out when necessary by the aid of a blast lamp. All tubes should have their edges rounded by rotating in the flame of a Bunsen burner or blast lamp. Connections are made by short lengths of rubber tubing, which should fit tightly and be worked on to each tube for one and a half or two centimetres from its end. All joints between rubber and glass are made more certainly gas-tight by the use of vaseline or of the grease described in the Appendix. It often happens that two tubes of different sizes are to be joined; in these cases the *adapters* described in the Appendix will be found very useful. In all connections the ends of the glass tubes should meet inside of the rubber tubing.

Tubes and flasks which have been washed are dried quickly by aspirating or blowing air through them while they are rotated in a low flame. The operation is shortened if, after draining off the water, they are rinsed out with a little alcohol.

Collecting and Measuring Gases. Some of the gases dealt with in this book are completely soluble in some solution, so that the weight of the gases given off in the reaction can be found by determining the increase in weight of the absorbent solution.

Others, practically insoluble, are collected over water or some solution in graduated tubes. Gas tubes of 200 cc. capacity are recommended for most of the experiments with gases in this book; but, of course, other sizes may be used, with a corresponding change in the conduct of the experiment.

The up-turned end of the delivery tube used in collecting gases should be kept on a level with the surface of the water outside the gas tube. After the gas is collected, the tube containing it is transferred to a deep glass vessel nearly filled with water at the room temperature, where it is allowed to stand for ten or fifteen minutes so that the solution over which it may have been collected shall diffuse into the water, and the gas acquire the temperature of the water. The tube is now held by a clamp or strip of cloth (the bare hand must not touch it) so that the levels of the water within and without are the same, and the volume of the gas is read by noting the lowest point of the concave meniscus. Care must be taken that the eye is on a level with the surface of the liquid in the tube so that errors due to parallax may be avoided.

Gases may also be collected over water in flasks (or ungraduated tubes) and the measurement made as follows: After adjusting the water levels as before, the flask is closed by a piece of paper held against its mouth by the fingers, and placed upright on the table. The water left in the flask is measured by pouring it into a graduated cylinder, and then the capacity of the flask is ascertained by measuring the water which will exactly fill it. The volume of the gas which was collected is, of course, the difference between these measurements. This is a comparatively rough method and inadvisable except when a large volume of gas must be dealt with.

Still another method for collecting gases over water which may be used for large volumes of gas, is the following: A bottle or flask of proper size is fitted as an aspirator (Fig. 22, Appendix), but with the outer limb of the longer tube only 3 to 4 cm. long. To this tube is attached a rubber tube bearing a pinch-cock and ending in a short glass tube drawn out to a small opening. The bottle is filled with water, the stopper inserted, a little water forced over through the siphon into a beaker, and the pinch-cock closed. The apparatus for generating the gas is next connected with the shorter tube and, with the siphon outlet under water and pinch-cock open, the beaker is raised till the levels of water in beaker and bottle are the same. The pinch-cock is then closed and the beaker emptied and replaced under the outlet. Now the pinch-cock is opened again and the experiment is carried out. When no more gas is to be collected, the levels of water are adjusted as before, the pinch-cock closed, and the water in the beaker measured. If heat has been used to produce gas,—as in making oxygen from potassium chlorate,—the apparatus should be allowed to cool before adjusting the levels. Measurement of the water in the beaker gives the volume of the gas.

At the time of measurement, the temperature of the water over which the gas stands, the height of the barometer and its temperature must, in most cases, be noted. From these data and the known weight of unit volume of the gas in question, the weight of the measured volume of gas may be calculated.

Methods for making the gases used in the experiments are given in the Appendix.

All substances used in the quantitative reactions,—those weighed for the determinations and those em-

ployed as reagents,—should be as pure as possible. Fortunately, many chemicals of guaranteed purity can now be purchased. If necessary, many of the salts may be purified by re-crystallization; oxides of a number of metals may be prepared by heating their re-crystallized nitrates; and several metals may be obtained pure by reduction of these oxides or salts. Distilled water should be used for diluting acids which are employed as quantitative reagents and in the few cases where precipitates are washed with water.

A number of determinations may be made in series, using the weighed product of one reaction as the starting point for another; in other cases, the product may be employed for a second determination, but must be reweighed, because the experiment is carried out in a different apparatus. A list of some of the possible series is given in the Appendix.

Before beginning an experiment, the directions should be read through carefully, so that the purpose and the details of each step shall be fully in mind from the start, and frequent reference to the book unnecessary.

II

CALCULATIONS

Calculation of the Normal Volume and the Weight of a Gas. As the weight of a cubic centimeter of a gas varies with its temperature, the pressure to which it is subjected, and the proportion of water vapor which is mixed with it, it is necessary, in finding the weight of a measured volume of a gas, to know the weight of a cubic centimeter under the conditions at the time of measurement; or to calculate what the volume would be under definite standard conditions, and multiply it by the weight of a cubic centimeter determined under these same conditions. The latter is the method always employed.

1. By the application of the laws of Boyle and of Charles, we calculate what the volume would be if the gas were dry, at the temperature of 0° C. and under a pressure of 760 mm. of mercury. This is called the *normal volume.*

Reduction to 0° C. By Charles' law the volume of a gas is proportional to its absolute temperature. Hence, if v is the volume measured at the temperature t, and v_0 the volume at 0°,

$$v_0 = v\frac{273}{273+t}.$$

Reduction to 760 mm. The standard pressure is 760 mm. at 0°. Since, in practice, the barometer is always

read at a higher temperature, the reading must be corrected for the expansion of the mercury and of the scale. A sufficient correction is made by subtracting from the reading in millimeters $0.13 \times t$ if the scale is on glass, or $0.12 \times t$ if on brass, t being the temperature of the barometer.

By Boyle's law the volume of a gas is inversely proportional to the pressure under which it stands. Therefore if v is the volume measured, b the corrected barometer reading, and v_{760} the volume at 760 mm.,

$$v_{760} = v \frac{b}{760}.$$

If the gas stands over water, it is saturated with water vapor, and the tension of this vapor makes the volume greater than if the gas were dry. The value of this tension depends on the temperature of the water (*cf.* table in the Appendix); and correction for it is made by subtracting its amount, expressed in millimeters of mercury, from the corrected barometric height. If w is the aqueous tension for the temperature at which the gas is measured, the corrections for barometric height and the presence of water vapor are made at once in the formula:

$$v_{760} = v \frac{b-w}{760}.$$

The corrections for temperature and for pressure are made successively in either order; or may be made simultaneously by using one of the following formulas, in which v_n represents the normal volume of dry gas:

$$v_n = v \frac{273(b-w)}{760(273+t)}, \text{ or } v_n = v \frac{b-w}{760(1+0.00367t)}.$$

2. Having found the normal volume, the *weight of the gas* is now obtained by multiplying this volume in cubic centimeters by the weight of 1 cc. of the gas under normal conditions. The latter may be found in the table in the Appendix, or readily calculated from the molecular formula of the gas and that of some other gas whose unit weight is known; for the densities of gases are to each other as the molecular weights.

Example. If the weight of 1 cc. of oxygen is known to be 1.43 mg., the weight of 1 cc. of carbon dioxide is found by the proportion:

Mol. wt. oxygen : mol. wt. carbon dioxide :: 1.43 : x

32 : 44 :: 1.43 : x

whence x = 1.966.

Calculation of the weight of substance to be used in reactions yielding a gas. This calculation is often necessary to avoid exceeding the capacity of the gas tube used for collection. Assuming the maximum temperature and the minimum pressure likely to prevail at the time of the experiment, the capacity of the gas tube is reduced to normal volume and the weight of the gas calculated. Then from the equation representing the reaction, the weight of the substance which will yield this weight of gas is determined.

Example. To find the weight of potassium chlorate which will give 200 cc. oxygen, measured over water at 20°, and with the barometer at 740 mm. (corrected).

$$v_n = 200 \frac{740 - 17.4}{760(1.0734)} = 177.15 \text{ cc.}$$

As 1 cc. oxygen under normal conditions weighs 1.43 mg., the weight of the gas which will fill the tube

under the stated conditions is 253.3 mg. The weight of potassium chlorate is found by the proportion:

$$48 : 122.6 : : 253.3 : x = 647.$$

Molecular Weights of Gases from their Densities. According to Avogadro's hypothesis, equal volumes of gases, when measured under like conditions of temperature and pressure, contain equal numbers of molecules. The relative densities of gases, therefore, express the relative weights of their individual molecules.

To translate the relative densities into molecular weights of the chemical scale, it is only necessary to select some established molecular weight for reference. *The molecular weight of oxygen = 32* is usually chosen.

Since the density of oxygen (air = 1) is 1.105, the *average molecular weight of air = 28.96*, for

$$1.105 : 1.000 : : 32 : 28.96;$$

and the molecular weight of a gas may be found from its density relative to air by the following proportion:

Density of air : density of gas : : 28.96 : mol. wt.;

or the molecular weight is equal to the density of the gas (air = 1) multiplied by 28.96.

Equivalents and Atomic Weights. (The subject of equivalents and atomic weights should be carefully studied in some good text-book.) The results of quantitative determinations give the ratios in which the constituents of compounds are combined, and from these ratios a list of relative weights may be made which will represent the combining weights or equivalents of the constituents. The equivalent may be defined as that amount of an element which combines with eight parts of oxygen or with an equivalent

weight of some other element or group. Thus (using approximate numbers), 16 parts of sulphur and 8 parts of oxygen, respectively, are found to combine with the same weight of silver. The equivalent of sulphur is, therefore, 16. But we find in some cases that an element appears to have more than one equivalent; for instance, a synthesis of sulphur dioxide, shows that 8 parts of sulphur combine with 8 parts of oxygen; analyses of three oxides of lead give as equivalent of lead the three numbers, 103.45, 77.6 and 51.72; determinations of the composition of the oxide of tin and of its hydrogen equivalent show that tin has two equivalents, 59.5 and 29.75; and analyses of the oxides of copper lead to the numbers 63.6 and 31.8 as equivalents of copper. In all such instances, the highest number is chosen as the equivalent.

The confusion arising from having two or more values for the equivalent of an element is done away with by the establishment of a table of atomic weights. The standard of atomic weights is $O = 16$, and the atomic weights of the other elements are either the same as their equivalents or some small multiple of them. The considerations which decide this point are not always simple ones. A knowledge of the molecular weight of the substance is of the first importance, but it is also necessary to know the number of atoms of each element in the molecule.

With gases the matter is not so difficult. For what appear good reasons (Gay Lussac's law of combination by volume, Avogadro's hypothesis, "nascent state," ratio of specific heats), the molecules of the common elementary gases are believed to consist of two atoms each. Hence the atomic weights of these elements must be one-half their molecular weights ($O = 32$) as found by density determinations.

In the case of compound gases whose volumetric composition is known, the numbers of atoms of each constituent in the molecule must be in the same ratio as the volumes in which they combine. An illustration in which the volume of one of the constituents is found indirectly is the following: An analysis of ammonia by copper oxide (p. 49) gave 4.63 as the equivalent of nitrogen (H = 1), and the molecular weight of ammonia was found to be 17. In a volumetric analysis of ammonia by chlorine (p. 51) the volume of nitrogen set free was one-third that of the chlorine used. But the combining volumes of hydrogen and chlorine are equal, hence we infer that the volumetric composition of ammonia is three volumes of hydrogen to one of nitrogen. This leads to the conclusion that there are three atoms of hydrogen and one atom of nitrogen in the molecule of ammonia and therefore the atomic weight of nitrogen is 14 or three times the equivalent found.

When the volumetric composition of a gas is not known, a certain amount of assistance is gained from its molecular weight. For instance: The equivalent of sulphur is found to be 16; the molecular weight of sulphur dioxide is 64, and it is composed of equal parts by weight of sulphur and oxygen.

Wt. of sulphur dioxide : wt. of sulphur : : 64 : units of sulphur in the molecule, or

$$2 : 1 : : 64 : 32,$$

which is the atomic weight of sulphur, *if there is but one atom of sulphur in the molecule of sulphur dioxide.*

We may conclude, further, that there are two atoms of oxygen in the molecule of sulphur dioxide,

for a like proportion gives the units of oxygen, and as its atomic weight is 16, two atoms make up this amount.

The decision in regard to the atomic weights in such instances as the above and in many others depends on considerations, which with one exception need not be given here.

Use of Specific Heats in Determining Atomic Weights. (For definitions of specific heat, etc., see page 37.) The specific heats of the solid elementary substances are, in general, inversely proportional to the atomic weights; or in other words, the product of specific heat and atomic weight is an approximately constant quantity, its values lying in the neighborhood of 6.4. (Law of Dulong and Petit.)

Knowledge of the specific heat of a solid simple substance may, therefore, be used to decide whether its equivalent is also its atomic weight or some submultiple of it. The procedure is this:

Multiply the equivalent by the specific heat; if the product is not far from 6.4, the equivalent and the atomic weight are the same; if the product is less, find what whole number as a multiplier will give the value nearest to 6.4, and the atomic weight is the equivalent multiplied by this whole number.

Examples. The equivalent of zinc (oxygen = 8) was found (p. 64) to be 32.6; its specific heat is 0.095, and the product 3.097. Hence the atomic weight of zinc is twice the equivalent, or 65.2 (65.4).

The equivalent of tin was found (p. 64) to be 29.42; its specific heat is 0.056, and the product, 1.647. $1.647 \times 4 = 6.588$; hence the atomic weight of tin is $29.42 \times 4 = 117.68$ (119).

The equivalents and atomic weights which are found from the results of the experiments in this book must be in most cases only rough approximations to the true values; but the experimental work and the calculations may serve to illustrate the methods and reasoning employed in exact determinations.

Derivation of the Formula of a Substance from the Figures which give its composition by Weight. If the figures which represent the proportion of each element by weight are divided by the atomic weight of this element, it is evident that the quotients will show the relative numbers of atoms of each element in the compound. If we reduce the ratio or ratios thus found to the lowest terms, the numbers will be those of the atoms in the simplest empirical formula.

For instance: the composition of sulphur dioxide was found (p. 54) to be,—sulphur = 49.55% and oxygen = 50.45%. Dividing these percentages by the atomic weights of the respective elements,

$$49.55 \div 32 = 1.548, \text{ and } 50.45 \div 16 = 3.155.$$

But 1.548 : 3.153 : : 1 : 2, (nearly); hence the simplest formula is SO_2.

The true formula might be, however, any multiple of this,—S_2O_4, S_3O_6, etc. To decide between these possible formulas, it is necessary to know the molecular weight. The density of sulphur dioxide with reference to air was found (p. 36) to be 2.24; therefore, since the average molecular weight of air is known to be 28.96, the molecular weight of sulphur dioxide is $2.24 \times 28.96 = 64.8$, and the right or molecular formula is SO_2. Where no evidence in regard to the molecular weight can be obtained, the simplest formula is generally used.

For instance: 840 mg. of iron oxide was found to contain 587 mg. of iron and 253 mg. of oxygen. Dividing these figures by the atomic weights, $587 \div 55.9 = 10.5$ and $253 \div 16 = 15.8$. These quotients are in the ratio of 2 : 3, very nearly, and hence the simplest and accepted formula is Fe_2O_3.

Either the figures expressing percentage composition or those which immediately express the results of the determination may, of course, be used for finding the atomic ratios,— as is seen in the examples given above.

III

THE GAS LAWS

1. **Boyle's Law.** To demonstrate that the volume of a gas is inversely proportional to the pressure under which it is confined.

Method. Air confined in a glass tube by mercury is subjected to different pressures by altering the height of the mercury column, and the length of the air column is measured.

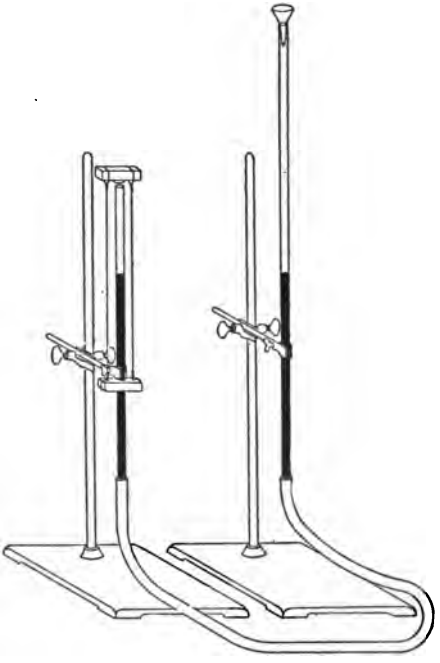

FIG. 1.

Apparatus. In place of the apparatus sold by the dealers, that shown in Fig. 1, and described below, may readily be made. The two glass tubes are about 5mm. in inside diameter and 40 cm. long. They are connected by stout red rubber tubing and the connections secured by binding with fine wire or linen thread. Two blocks of wood 4 cm. long, 2.5 cm.

wide and 1 cm. thick are made. A small rubber pad about 1.5 cm. in diameter is cut from a rubber stopper and fastened to the middle of the face of one of the blocks with sealing wax. Through the center of the other block a hole is bored, slightly larger than the glass tube, and a very small hole near each end. Two pieces of No. 20 copper wire are threaded through the small holes in the second block and made fast, and loops large enough to receive the first block are made in both wires at the same distance, about 25 cm., from the fastened ends. The second block is now slipped over the air tube and brought below the clamp, and the wire loops placed over the ends of the first block, which are notched to receive them.

Both tubes being clamped vertically, mercury is poured in until it half fills them, and any air which may have been caught in the rubber tube is expelled by hanging the tube over the edge of the table and pinching it.

The quantity of air desired for a series of determinations is confined in the air tube by adjusting the mercury to the right height, placing the rubber pad on the top of the tube, pushing the tube up in the loosened clamp against the pad with considerable force, and then clamping tightly. The pad should be covered with a film of glycerine or grease.

Experiments. The experiments are naturally divided into two series,—those in which the pressures are greater than the barometric pressure, and those in which they are less.

First series. By raising or lowering one of the tubes while the air tube is open, bring the mercury nearly to the bottom of this tube. Close the tube and measure the length of the air column and the height

above the table of the mercury in the tubes. Now lower the stand holding the air tube to three or four new positions,—to a stool, a chair, a box, and finally to the floor. In each position measure the length of the air column and also the difference in height of the mercury in the two tubes. The mercury levels are best measured from the top of the table as a plane of reference.

Second series. Adjust the air under barometric pressure to fill somewhat less than half the tube, and read the length of the air column and the difference in the mercury levels as before, for several positions in which the air tube is the higher.

Read the barometer at the time of the experiments.

Calculation. At the start of each series of measurements the inclosed air is under the existing atmospheric pressure. In each new position in the first series, the pressure is measured by the sum of the barometric height and the difference in the mercury levels; in the second series, by the barometric height less this difference.

As the air tube is assumed to be cylindrical, the length of the air column is proportional to the volume of the air and serves to represent it. The temperature of the room will probably remain unchanged during a series of measurements; otherwise, a temperature correction is necessary. In both series of experiments, the products of volume (length) by the corresponding pressure should be very nearly the same. The data should be plotted on coördinate paper, with volumes as abscissas and pressures as ordinates, and a line drawn through the points thus located.

2. Charles' Law. To demonstrate that, under like conditions of pressure, the volume of a gas is proportional to the absolute temperature.

First Method.

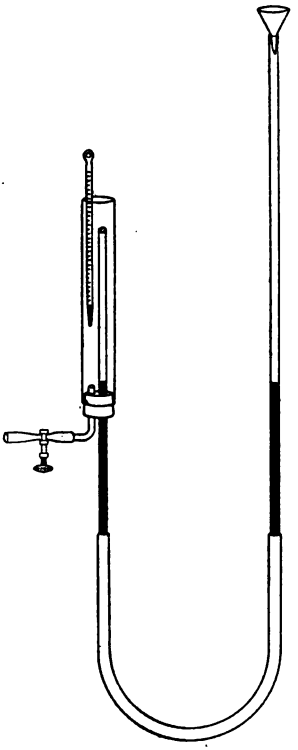

FIG. 2.

Apparatus. Two glass tubes like those used in the Boyle's law apparatus are connected by about 40 cm. of thick-walled red rubber tubing, and the connections secured with fine wire. A glass cylinder, 4 cm. in diameter, is fitted on one of the tubes as shown in Fig. 2. This tube is to serve as the air tube, and is closed during the observations by a small rubber stopper. The other tube is for the purpose of adjusting the pressure before each reading. Mercury is poured into the apparatus, until it stands a few centimeters high in both tubes. Air caught in the rubber tube is removed by pinching.

In order to fill the air tube with dry air, a calcium chloride tube is connected with it by a rubber stopper, the cylinder filled with hot water, and the mercury caused to rise and fall to the top and the bottom of the tube several times. The

hot water is then withdrawn, and the mercury adjusted at about 25 cm. from the top of the air tube. When the tube has cooled, the drying tube is removed and the air tube immediately closed by the small stopper.

Experiment. Fill the cylinder with ice water containing some pieces of ice. Stir the water with a glass rod until no further change in the air column occurs; then take the temperature of the water and raise the leveling tube so that the mercury is at the same height in both tubes. Measure the length of the air column by a metric rule placed in the water close to one side of the tube. Make similar adjustments and readings with the cylinder filled with water at different temperatures, and, finally, while a rapid current of steam is driven through the bent tube at the bottom of the cylinder, its top being loosely closed by a large cork or a piece of asbestos board.

It is advisable during the experiment to move the air tube through the cork when necessary, so that the mercury only just shows above the cork; otherwise, the heating of the mercury may disturb the results.

Calculations. As in the Boyle's law experiments, the air tube is supposed to be cylindrical, and hence the lengths of the air column represent volumes. These volumes are measured in each case under atmospheric pressure, which usually will not change during a series of observations. Each of the observed volumes is divided by the corresponding temperature changed to readings of the absolute scale by adding 273. The quotients should be a nearly constant quantity.

With the volumes as abscissas and the temperatures in centigrade degrees as ordinates, the results should

be plotted. It will be seen that the line, connecting the points thus located, if continued, will pass near the point for temperature —273° and volume 0.

Second Method.

Apparatus is shown in Fig. 3. The air tube is not more than 1.5 mm. in inside diameter, and about 60 cm. long. As it is important that this tube be of uniform section, and as most small tubes are apt to be conical rather than cylindrical, it must be selected with some care. Promising pieces about 65 cm. long are tested by drawing into them a thread of mercury about 10 cm. long and observing its length in different parts of the tube. If this shows much variation, the tube is rejected.

FIG. 3.

When a suitable tube is found, it is cleaned and dried. It is then connected with a calcium chloride tube at each end and heated while a current of dry air is aspirated through it for a few minutes. Without disconnecting, it is sealed as near to one end as possible by means of the Bunsen flame. It is now heated again to expand the air, and when quite hot, the open end is disconnected and quickly plunged beneath the surface of clean, dry mercury. When a thread of mercury about 2 cm. in length has been drawn into it, the tube is taken out of the mercury and allowed to cool completely. The mercury index is then run down to a position about two-thirds the length of the tube from the closed end by the aid of a fine iron wire, and a thermometer tied to the tube with fine wire. Tube and thermometer are inclosed in a jacketing tube 2 cm. in diameter and

somewhat longer than the air tube, as shown in Fig. 3.

Experiment. Clamp the apparatus in a vertical position with a meter stick, and siphon water of any desired temperature through it. Finally drive steam through it. At each temperature record the length of the air column and the thermometer reading. The calculations are the same as in the first method.

Third Method.

Charles' law may also be demonstrated indirectly, by the aid of Boyle's law, from determinations of the relations of temperature to pressure while the volume remains constant. The method is that of the air thermometer.

Apparatus. As shown in Fig. 4, the apparatus consists of a 250 or 300 cc. flask fitted with a rubber stopper, through which passes a heavy-walled glass tube of small bore, bent twice at right angles, and a short tube with a glass stop-cock or with a piece of heavy rubber tubing provided with a screw clip. The stopper should be wired to the neck of the flask. A file mark is made for reference on the vertical limb of the heavy-walled tube as shown, and a leveling tube is connected by a 50 cm. length of stout red rubber tubing, which is secured to the tubes by ligatures of wire or thread.

A calcium chloride tube is connected with the short tube, and air is aspirated through the apparatus for five or ten minutes, while the flask is gently heated and allowed to cool. Mercury is then poured into the open tube until it stands about 3 cm. high in each tube.

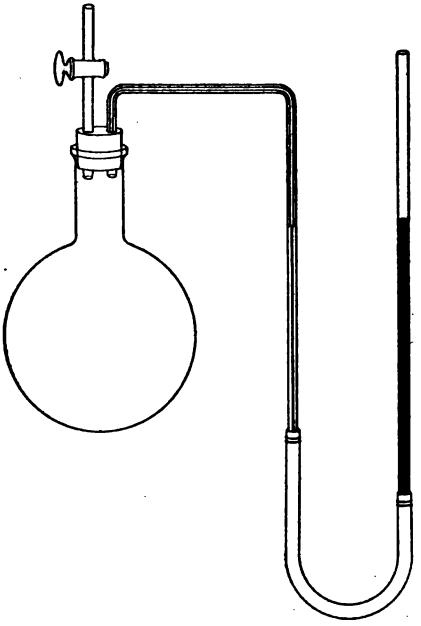

FIG. 4.

Care must be taken to expel any air that may be in the rubber tube.

Experiment. Immerse the flask completely in ice water which contains some ice and stir till, with the cock closed, the height of the mercury in the tube remains constant. Now open the cock, adjust the mercury to the file mark by means of the pressure tube, and close the cock. Measure from the table the height of the mercury in the open tube and read the barometer. Now replace the ice water by water of room temperature, bring the mercury to the file mark as before, and record the temperature of the water and the height of the mercury in the pressure tube. Make similar observations at intervals of twenty degrees up to the boiling point, holding the temperature constant each time by regulating the flame of the burner.

Calculations. The air at the first observation is at 0° and under atmospheric pressure. At each higher

temperature, a greater pressure is necessary to bring it back to the original volume. By adding to the barometer reading the several differences between the heights of the mercury in the pressure tube and its initial height, we have a series of pressures corresponding to the several temperatures of the constant volume of air at which the pressures were observed.

On inspection of the figures, it will be seen that, if the absolute scale of temperature is used, the quotients obtained by dividing the temperatures by the pressures are nearly a constant quantity — that is, *at constant volume the pressure is proportional to the absolute temperature.* Now since by Boyle's law, volumes are inversely as pressures, it follows that if the pressures had been constant throughout the experiment, the volumes would have been directly proportional to the absolute temperature. For, since p varies as $\frac{1}{v}$ (Boyle's law), and p varies as T; p varies as $\frac{T}{v}$, or pv varies as T.

IV

THE DENSITIES OF GASES

The density of a substance is the weight of its unit volume,—one cubic centimeter. Specific gravity is the ratio of the weight of a definite volume of a substance to the weight of an equal volume of some standard substance. The term density, or more properly relative density, is however commonly used in the case of gases to designate specific gravity. The standard for the relative density of a gas is usually air.

While the exact determination of the density of a gas is a difficult problem, it is possible by simple methods to obtain approximate results which are sufficiently accurate to serve as a basis for fixing molecular weights.

3. **Weight of a Cubic Centimeter of Air.** *First Method.* A flask is weighed full of air, and again when the air has been partly removed. The volume of the air whose weight is thus found is measured by the volume of water which enters the flask when it is opened under water.

Apparatus. A round-bottomed flask of 250 to 300 cc. capacity is fitted as shown in Fig. 5 with a rubber stopper through which passes a glass tube, projecting 2 to 3 cm. A short piece of heavy rubber tubing fits over this projecting tube and carries a

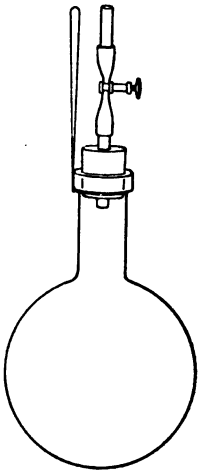

FIG. 5.

screw pinch-cock. A loop of fine wire is fastened to the neck of the flask for convenience in weighing. A glass stop-cock may be substituted for the rubber tube and clamp. A vessel large enough to contain the flask is also provided.

Experiment. Weigh the clean, dry flask with its fittings, suspending it from the hook over the balance pan and leaving the tube open. Note the temperature of the air near the balance and the height of the barometer. Withdraw the air from the flask as completely as possible by a water aspirator or air pump, and close the pinch-cock. Weigh again, and then bring the flask mouth down into a vessel of water of room temperature, and open the pinch-cock. (The water must be in a vessel large enough to allow it to completely cover the flask.) When no more water enters the flask, bring the surface of the water in the flask to the level of that outside and, closing the rubber tube with the fingers, remove the flask and set it upright on a ring. Take out the stopper, allowing the water in the tube to drop into the flask, and measure the water by pouring it into a graduated cylinder.

Calculation. The difference in the weights of the apparatus is the weight of the air whose volume is equal to that of the measured water. The weight of 1 cc. of the air of the room, under the conditions at the time of the experiment, is found by the proportion:

Vol. measured : 1 : : wt. found : wt. of 1 cc.

The weight of a normal cubic centimeter of air can be found by correcting for temperature and pressure, as described on pages 7 and 8.

Second Method. Air is expelled from a flask by steam and the closed flask weighed; air is then admitted and the flask again weighed. The volume of the air whose weight is thus found is determined by measuring the water still in the flask and subtracting this volume from the capacity of the flask.

Apparatus is that used in the first method, with a glass tube about 35 cm. long and bent at an acute angle near one end.

Experiment. Put about 80 cc. of water in the flask. Connect the flask with the bent tube, support it for heating, and bring the end of the bent tube into a large beaker of water. Boil the water (use a small flame to avoid cracking the flask) till no more bubbles of air appear in the beaker. The boiling must be continuous else the water in the beaker will suck back. When the air is all expelled, withdraw the flame and immediately close the pinch-cock. After the flask has cooled to room temperature, weigh it, open the pinch-cock, and weigh it again. Take the temperature of the water which remains in the flask and measure its volume. To find the capacity of the flask, fill it completely with water, push in the stopper, with the pinch-cock open, to the same point as before, then withdraw it and measure the water.

Calculation. The difference of the two weights is the weight of the air whose volume is equal to the capacity of the flask less the volume of water left

after the boiling. But this air was saturated with moisture. To find the volume of dry air contained in the measured volume of moist air, the following proportion is used,— in which b is the barometer reading, w the aqueous tension for the temperature of the water in the flask, and v the measured volume:

$$b : b - w :: v : \text{volume of dry air.}$$

The weight of 1 cc. of air under normal conditions is now found as described under the first method.

4. Weight of a Cubic Centimeter of Oxygen. Oxygen from a weighed amount of potassium chlorate or mercuric oxide is collected over water and its volume measured. Its weight is the loss in weight of the substance. From these figures the weight of a cubic centimeter under normal conditions is calculated.

Apparatus. An ignition tube of hard glass, about 15 cm. long and 9 mm. in inside diameter, connected with a gas delivery tube by an adapter and rubber tubing, as shown in Fig. 6; a 200 cc. graduated gas tube.

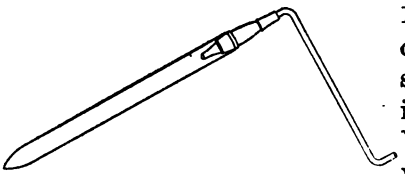

FIG. 6.

1. *Experiment.* Powder finely some potassium chlorate, and dry it by gentle heating. Weigh in the previously weighed ignition tube from 600 to 640 mg. of the salt. Make the connections gas-tight and clamp the tube at an inclination of about 45° at a convenient height for heating. Fill the gas tube with water, invert it in a dish of water, and clamp it in position. Bring the delivery tube under the gas

tube and begin to heat the salt. Heat cautiously at first at the surface of the salt, and prevent, as far as possible, the creeping up of the melted salt on the walls of the tube. At the last, heat strongly, and when no more gas is evolved, disconnect the delivery tube.

Transfer the gas tube to a deep cylinder of water at room temperature for adjustment of temperature and measurement, and weigh the ignition tube when it has cooled. Read the volume of the oxygen in the manner described on page 4, and note the temperature of the water over which it stands and the height of the barometer.

Since the tube was cool at the start and hot at the end of the experiment, a portion of the gas collected is due to expansion in the tube. To make an approximate correction for this expansion, see how much gas (air) can be collected by heating the cold ignition tube to the end temperature of the experiment, and subtract this from the observed volume.

Calculation. Reduce the gas to normal volume, and find the weight of 1 cc. by dividing the volume ~~by~~ into the loss in weight of the tube.

From the data of this experiment, calculate also the percentage of oxygen in potassium chlorate.

2. *Experiment.* Dry some mercuric oxide by heating it slightly above 100° for a short time, or by keeping it in a desiccator over concentrated sulphuric acid for a day or two. Weigh in an ignition tube, of the form shown in Fig. 7, and 15 cm. long, about 3 g. of the oxide, place in the upper part of the tube a loose

FIG. 7.

wad of long-fibered asbestos which has just been ignited by holding it with the forceps in the Bunsen flame, and weigh again; or weigh the oxide on a watch glass and transfer to the unweighed tube, add the asbestos and weigh the tube. Support the tube in a nearly horizontal position and proceed as in the case of the chlorate, being careful, however, to heat the tube as little as possible beyond the oxide. Heat till the oxide has all disappeared. Correct for expansion as in 1.

Calculation. The weight of 1 cc. of oxygen is found as in the last experiment. The results may also be used to determine the equivalent of mercury, the percentage composition of mercuric oxide and its formula.

5. Weight of a Cubic Centimeter of Hydrogen. This is determined as in the case of oxygen by finding the loss in weight in a reaction which gives a measured volume of the gas.

Apparatus. A conical flask of about 150 cc. capacity fitted with a rubber stopper carrying a small drying tube filled with granulated calcium chloride (Fig. 8); a delivery tube connected with this by rubber tubing; a liter flask for the collection of the gas; and a vessel of water large enough to contain the flask and serve as a pneumatic trough.

Experiment. Put about 60 cc. of dilute sulphuric acid (1 : 10) in the flask. Weigh about 2.5 grams of pure zinc, and then weigh the metal with the flask and drying tube. Place the flask in water to prevent heating during the reaction, connect the delivery tube

and bring its end under the mouth of the liter flask, which has been filled and inverted over water. Now remove the stopper, drop the metal into the acid and quickly re-insert the stopper.

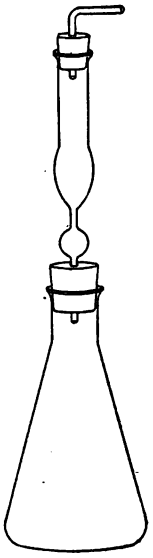

FIG. 8.

When the metal has entirely disappeared, disconnect the delivery tube, wipe the small flask dry, remove the stopper and flush the hydrogen out of the drying tube by aspirating air through it for a minute or two. Replace the stopper and weigh. Adjusting the levels of the water in the liter flask and in the trough, close the mouth of the flask with a piece of paper held in place by the fingers, and set the flask upright on the table. Measure the water remaining in the flask, and find the capacity of the latter by measuring the water necessary to fill it. The difference of these measures is the volume of the hydrogen which was collected. Take the temperature of the water in the trough and read the barometer.

Calculation. Reduce the volume to normal and find the weight of 1 cc. as in the case of oxygen by dividing the volume by the loss in weight of the flask and drying tube.

The results are likely to be too high as the hydrogen evolved by the metal is usually not quite pure. It is advisable to use the purest zinc and to add a few drops of copper sulphate solution to the acid.

6. Determination of Relative Densities of Gases. The most direct method of finding the relative density of a gas is by weighing equal volumes of the gas in question and of the standard gas. The gases must,

of course, be weighed at the same temperature and pressure, or else the weight of one must be corrected to the temperature and pressure of the other. Instead of actually weighing the standard gas, the weight of the equal volume may be calculated from the known weight of 1 cc. In this case, either the weight of the standard gas (usually recorded for normal conditions) must be corrected to the conditions under which the other gas was weighed, or the volume of the latter reduced to normal. For instance,—340 cc. of sulphur dioxide at 20° and with the barometer at 750 mm. were found to weigh 898 mg. To find the density relative to air: 1 cc. of air under normal conditions weighs 1.293 mg.; this corrected to 20° and 750 mm. becomes 1.189 mg., and the weight of 340 cc. would be 404 mg. The relative density of sulphur dioxide with reference to air is therefore $898 \div 404 = 2.22$. Or, reducing the volume of the sulphur dioxide to normal, it becomes 313 cc.; and the weight of 313 cc. of air under normal conditions (313×1.293) is 404 mg. Therefore the relative density is $898 \div 404 = 2.22$ as before.

The apparatus for the determinations consists of a Chancel specific gravity flask (Fig. 9) or a conical flask of about 300 cc. capacity, fitted as shown in Fig. 10. The rubber tubes are closed by screw pinchcocks, or, to avoid extra weight, by plugs of glass tubing (Fig. 10, B).

The capacity of the flask is found, once for all, as follows: Fill it completely with water and insert the stopper with the tubes open. Mark with a fine file on the neck of the flask the position of the bottom of the stopper. (This is unnecessary when using the Chancel flask.) Insert the glass plugs, or close the

pinch-cocks and remove the water which may be in the rubber tubes beyond them; then open the tubes and let the water in them drain into the flask. Measure the water, or determine its volume by weighing it. Clean and dry the flask (*cf.* p. 3) and its fittings, and make all joints gas-tight with a little grease.

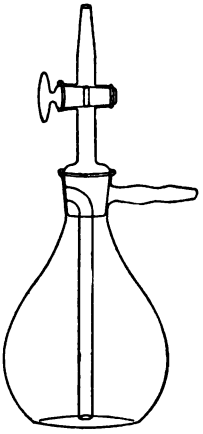

FIG. 9.

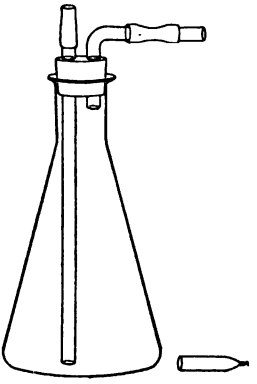

FIG. 10. B

Now aspirate air dried by a calcium chloride tube through the flask for five or ten minutes, leading the air in through the long tube. Disconnect and close both tubes. Be careful, in this and subsequent determinations, that the gas in the flask is under atmospheric pressure when the tubes are closed, and not expanded by the aspirator or compressed by the pressure of gas from a generator. Note the temperature near the flask while filling it and the barometer reading. Weigh the flask. Calculate the weight of the air in the flask under these conditions and subtract it from the weight just obtained. This gives the

weight of the *empty* flask which must be recorded for use in all of the following density determinations.

Experiments. Directions for making the gases are given in the Appendix. Fill the flask as directed in each case, and weigh. Note the temperature near the flask while filling it, and read the barometer.

Calculation. Subtract from the weight of the flask full of gas the weight of the empty flask. This gives the weight of a known volume of the gas under the temperature and pressure conditions of the experiment. The relative density or specific gravity of the gas is found by dividing this weight by the weight of an equal volume of air (or other gas which may be taken as the standard) under like conditions (*cf.* example p. 32).

The density proper, or weight of 1 cc., may also be found by dividing the weight of the gas by its volume.

After the experiments with chlorine, hydrogen chloride, ammonia, nitric oxide, hydrogen sulphide, and sulphur dioxide, the flask should be flushed out by a current of dry air.

1. *Density of Hydrogen. Apparatus.* Connect a hydrogen generator with a small wash bottle containing potassium permanganate solution and a calcium chloride tube, or wash bottle partly filled with concentrated sulphuric acid. Lead a rapid current of the purified and dry gas through the flask, connecting with the longer tube and supporting the flask mouth down for the better displacement of the air by the light hydrogen. After 8 or 10 minutes, disconnect and immediately close the flask, and weigh. Now lead the gas through the flask again for 5 minutes and weigh. Repeat if necessary till the weight is nearly constant.

The results are almost always somewhat too high on account of the difficulty of completely purifying the hydrogen from heavier gases, and its rapid diffusion.

2. *Density of Oxygen.* Wash the oxygen, if made from potassium chlorate, with water containing a little sodium hydroxide, and dry it by calcium chloride or sulphuric acid. If it is generated by heating, use a second wash bottle of water to cool it. Proceed as in Experiment 6, 1, but with the flask mouth upward while filling. Repeat to constant weight.

3. *Density of Nitrogen.* Make "atmospheric nitrogen" by leading air, freed from carbon dioxide by a tube filled with fragments of potassium hydroxide, through a tube containing granulated copper oxide, which is heated to a dull red. Wash and cool the gas by water, and dry it by calcium chloride or sulphuric acid.

Or make "chemical nitrogen" by one of the methods described in the Appendix, and cool and dry it as above. Repeat to constant weight.

4. *Density of Chlorine.* Wash and cool the chlorine from the generator by water, and dry it with concentrated sulphuric acid. Pass the gas through the flask and lead the issuing gas into a beaker of sodium hydroxide solution. Repeat to constant weight.

5. *Density of Hydrogen Chloride.* Dry the gas with sulphuric acid and lead it through the flask into a dilute solution of sodium hydroxide. Continue the current of gas till no more bubbles escape from the delivery tube, being careful that the solution does not suck back. It is not necessary in this case to lead the gas through the flask a second time, as it is evident that all of the air has been displaced.

6. *Density of Ammonia.* Support the flask mouth downward. Dry the gas by passing it through a tube filled with potassium hydroxide or soda-lime, and lead it through the flask into a dilute solution of sulphuric acid until absorption is complete. See that the evolution of the gas is continuous so that the acid solution does not enter the flask. It is unnecessary to repeat.

7. *Density of Hydrogen Sulphide.* Generate the gas from antimony sulphide (stibnite), wash with water and dry it with calcium chloride. Lead the gas through the flask into a solution of sodium hydroxide. Repeat to constant weight.

8. *Density of Nitric Oxide.* Wash and cool the gas with water and dry it with calcium chloride. Lead the escaping gas under a hood. Repeat.

9. *Density of Sulphur Dioxide.* Wash the gas with water and dry it with sulphuric acid. Lead the gas through the flask into a solution of sodium hydroxide until it is completely absorbed. Do not repeat.

10. *Density of Carbon Dioxide.* Wash with water and dry with calcium chloride. Lead the gas through the flask into a strong solution of sodium hydroxide until absorption is complete. Do not repeat.

11. *Density of Carbon Monoxide.* Wash and cool the gas with a solution of sodium hydroxide and dry it with calcium chloride. Burn the gas which issues from the flask at the end of a connected tube. Repeat to constant weight.

12. *Density of Acetylene.* Place the generating flask in water to keep it cool, and dry the gas with calcium chloride. Repeat to constant weight.

Calculate the molecular weights of the gases whose densities are determined (*cf.* p. 10).

V

SPECIFIC HEATS

The specific heat of a substance is the quantity of heat necessary to change the temperature of one gram through one degree Centigrade. The thermal unit is the specific heat of water.

A simple method for determining specific heats of solids is to bring a weighed amount of the solid, heated to a noted temperature, into a weighed amount of cold water, and observe the rise of temperature which occurs. At this point, the water and the solid have both reached the same temperature, and the water has gained as much heat as the solid has lost. The number of thermal units gained by the water equals its weight in grams multiplied by the number of degrees its temperature has risen. This divided by the product of the weight of the solid by its change in temperature, is the specific heat of the solid.

Since the vessel containing the water and the stirring rod are heated with the water, a correction is made for this loss from a knowledge of their specific heat and their weight. A correction for the loss of heat by radiation is avoided by starting with the water about as much below the room temperature as it will be above at the end of the experiment.

7. **Specific Heats of Metals.** *Apparatus.* A 400 cc. beaker standing on three small corks; a glass stirring rod; a vessel for boiling water; and a thermometer with wide graduation.

Experiment. Weigh on a trip balance the beaker and stirring rod together, then weigh in the beaker about 200 grams of water which has been cooled a few degrees below the temperature of the room, and place the beaker on the corks. Weigh the metal in sheet form, loosely coiled, or in a single lump, taking about 300 grams of lead, tin, cadmium, antimony, bismuth or silver; 200 grams of copper, zinc, iron or nickel; 100 grams of aluminium or magnesium. Tie a stout thread to the weighed metal and suspend it for 5 to 10 minutes in boiling water, noting the temperature. Now take the temperature of the water in the beaker, transfer the metal to the beaker and stir the water, recording the highest temperature it reaches.

Mercury (which has nearly the same specific heat in the liquid as in the solid condition) and metals in small pieces (*e. g.* copper turnings, granulated zinc, etc.) may be heated in a tin cup or in a beaker on a water bath or over a burner. In this case take the temperature of the metal just before emptying it into the water. Use about 300 grams of mercury.

The experiments may be made on a smaller scale, but the results are not likely to be as satisfactory.

Calculation. The "water equivalent" of the beaker and stirring rod is found by multiplying the specific heat of glass, which may be taken as 0.161, by their weight. This is then added to the weight of the water. If w is the corrected weight of the water, m the weight of the metal, t and t_1 the initial temperatures of the water and of the metal respectively, and t_2 the end temperature, the specific heat of the metal is:

$$s = \frac{w(t_2 - t)}{m(t_1 - t_2)}.$$

VI

ANALYSIS OF AIR AND COMPOSITION OF WATER

8. Composition of Air by Volume. *First Method.* Air displaced from a flask by a measured quantity of water is driven over heated copper, and the residual gas collected over water and measured.

Apparatus. A 300 to 400 cc. flask, fitted as shown in Fig. 11 (p. 40). The funnel serves as a dropping funnel (*cf.* Appendix), and may be conveniently replaced by a stoppered separatory funnel. A reaction tube of hard glass about 18 cm. long and 8 mm. in inside diameter (*cf.* Appendix); a gas delivery tube, and a 200 cc. gas tube.

Experiment. Place in the tube enough granulated copper or tightly rolled copper gauze to occupy about 10 cm. of its length, and hold the copper in position at equal distances from either end by loose plugs of asbestos. Connect one end of the tube with the flask and the other with the delivery tube. Place a screen of cardboard between the burner and the flask, and heat the copper to a dull red. While it is heating, arrange the gas tube for collecting the gas, and measure in a graduated cylinder 245 cc. of water. When no more air bubbles from the delivery tube, allow a little water to run into the flask slowly; then place the delivery tube under the gas tube with its end on a level with the water in the dish, and keep the water at this level during the experiment. Now

with the funnel closed, pour into it part of the measured water and allow it to run slowly into the flask. Add the rest of the water in successive portions, and be careful that no air is carried down with it into the flask. When all the water has run into the flask, read the volume of the gas which has been collected, with the proper adjustment of water levels.

Calculation. The measured water has driven over the copper a volume of air equal to its own; the oxygen has been fixed by the copper, and the gas collected consists of nitro-

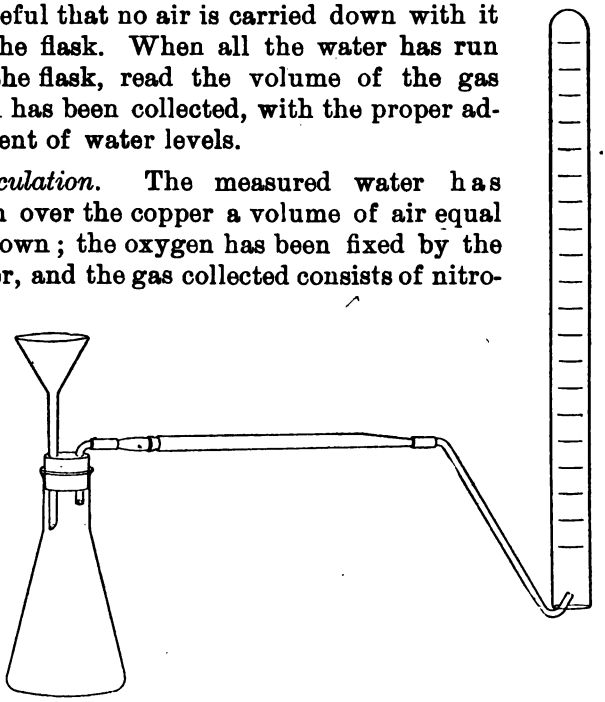

FIG. 11.

gen and argon. As the temperature of the air and of the residual gas are assumed to be the same, as both are saturated with moisture, and as the atmospheric pressure will not have changed sensibly during the experiment, no corrections are necessary. Find the percentage of oxygen by volume.

Second Method. The oxygen is removed from a measured volume of air by phosphorus.

Experiment. Pour enough water into a gas tube to stand at or a little above the lowest graduation when the tube is inverted with its end closed. Bring the end of the tube into a dish of water and clamp it in a vertical position. The water should all be of room temperature. Let the tube stand for a short time, and meantime fix a small piece of phosphorus on the end of a wire about 40 cm. long by melting the phosphorus in a little warm water, putting the end of the wire into it, and pouring in cold water till it has solidified.

Now adjust the level of the water in the gas tube, and, after reading the volume of the enclosed air, bring the phosphorus by aid of the wire into the upper half of the tube. The action is slow and it may be a day or more before it is complete. When there is no further evidence of action, withdraw the phosphorus, adjust the water levels, read the volume, and note the temperature of the water and the barometer reading. If the temperature and pressure are not the same as at the beginning of the experiment, the volume is corrected to these conditions. As both the air and the residual gas are saturated with moisture, no correction for aqueous tension is necessary. Find the percentage of oxygen in air by volume.

9. **Analysis of Water.** Steam is passed over heated iron or magnesium and the hydrogen collected. From the weight of the hydrogen and the gain in weight of the metal, the composition of water is determined.

Apparatus. A hard glass reaction tube about 18 cm. long, one end of which is drawn out as shown in Fig. 12; a 250 cc. conical flask, fitted with a tube bent to a

slightly obtuse angle; an adapter with one end drawn out to a length of 2 to 3 cm.; a 200 cc. gas tube, and a gas delivery tube.

1. *Experiment.* Place a loose wad of asbestos in the reaction tube about 6 cc. from the small end, and then bring into the tube enough fine iron filings, free from oil, to occupy about 5 cm. of its length, holding them in place by another asbestos wad. Tap the tube horizontally on the table to settle the filings and leave a small space above them. (If this precaution is not taken, the steam may drive the filings to the end of the tube and stop it up.) Heat the tube gently till it is perfectly dry. When the tube is cool, weigh it. Now connect it with the flask as indicated in Fig. 12, the long end of the adapter projecting 2 to 3 cm. into the tube, and support the reaction tube with its forward end about 2 cm. higher than the other, so that any condensed water will flow back into the pocket formed at this end. Connect the delivery tube and bring its end under the water in the dish in which the gas tube stands, but not under the gas tube.

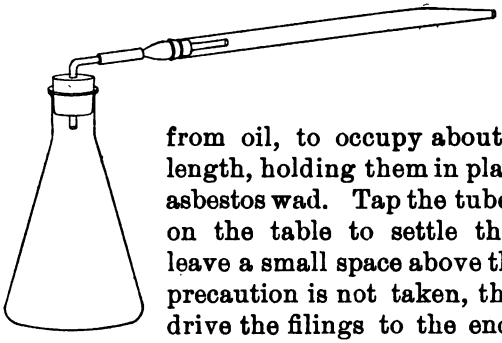

FIG 12.

Drive steam through the tube, heating the latter cautiously to evaporate the water which at first appears about the filings. When no more air comes from the delivery tube, place its end under the filled and inverted gas tube, and heat the iron strongly. After some 160 cc. of gas have collected, stop heating, but continue the current of steam till no more gas

is delivered, being careful that the water does not suck back and spoil the experiment. Disconnect the tube, dry it, and weigh it when cool. Measure the hydrogen with the usual precautions, and find its weight.

2. *Experiment.* Use magnesium ribbon instead of iron filings. The procedure is exactly the same as in the last experiment, except that a little less than 200 mg. of magnesium must be taken. The tube usually cracks at the end of the reaction, but this seldom prevents satisfactory results.

The gain in weight of the tube is the weight of the oxygen which was combined with the collected hydrogen. Calculate the equivalent of hydrogen (oxygen = 8), the percentage composition of water, and find its formula.

Example. Gain of magnesium (oxygen) = 103.00 mg.
Weight of hydrogen = 13.08

Weight of water decomposed = 116.08

Percentage of oxygen in water = 88.73 %; of hydrogen = 11.27 %. Equivalent of hydrogen (oxygen = 8) = 1.015. Empirical formula for water (H = 1; O = 16):

$$\frac{88.73}{16} = 5.55 \text{ and } \frac{11.27}{1} = 11.27,$$

and as 5.55 : 11.27 : : 1 : 2 (nearly), the formula is H_2O.

10. **Synthesis of Water.** Hydrogen is led over heated copper oxide and the water which is formed is absorbed by calcium chloride. The composition of water is found from the loss in weight of the copper oxide and the gain of the calcium chloride.

Apparatus. A hydrogen generator; a reaction tube; and two calcium chloride tubes (Fig. 13).

1. *Experiment.* Load the tube as in 9, but with 4 grams of fine copper oxide. Prepare it for weighing by heating the oxide in a current of air for 5 or

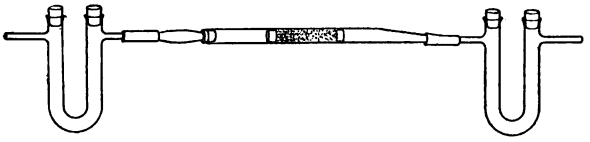

FIG. 13.

10 minutes. When it is cool, weigh it, and also weigh one of the calcium chloride tubes. Except when weighing the calcium chloride tube or using it in the experiment, keep it closed by short pieces of rubber tubing and plugs of glass rod. Connect the apparatus as shown in Fig. 13, the weighed calcium chloride tube with the small end of the reaction tube, and support the reaction tube so that this end is a little lower than the other. Connect with the hydrogen generator, and, when the air is displaced (test the gas issuing from the calcium chloride tube by collecting in a test tube over water and igniting), begin heating the copper oxide nearest the generator and continue till most of it is reduced. Let the tube cool in the current of hydrogen, and, while cooling, drive off any water which may be in the tube by cautious heating. When it is cool, disconnect the generator and aspirate air through the apparatus for five minutes to displace the hydrogen. Weigh the reaction tube and the calcium chloride tube. Calculations as in 9, 1.

2. *Experiment.* By slightly varying the last experiment, the composition of copper oxide may be determined with that of water in one operation.

Ignite the asbestos for the forward wad in the reaction tube by holding it with the pincers in the Bunsen flame, put it in position, and weigh the tube. Introduce the copper oxide, heat for a few minutes in a current of air, and weigh again when cool. Omit the second asbestos wad. Proceed as in the other experiment, but continue heating the copper for five minutes after it seems to be all reduced.

As the weight of the copper oxide is known and it is completely reduced to a known weight of copper, the equivalent of copper, the percentage composition of copper oxide, and its empirical formula, may be calculated, as well as the corresponding facts in regard to water.

VII

COMPOSITION OF SEVERAL GASES

11. **Analysis of Hydrogen Chloride.** Hydrogen chloride is led over heated iron and the hydrogen collected over water. The chlorine is fixed by the iron.

Apparatus. A hydrogen chloride generator and wash bottle with concentrated sulphuric acid; a reaction tube; a 200 cc. gas tube, and a delivery tube.

Experiment. Put half a dozen small, bright wire nails in the reaction tube and weigh. Connect the tube with the source of dry hydrogen chloride and a delivery tube, and lead the gas through the apparatus till it is completely absorbed in water at the end of the delivery tube. Now place the delivery tube under the gas tube and heat the iron. When about 180 cc. of gas have collected, withdraw the heat, but continue the current of hydrogen chloride till no more gas collects. (Be careful that the water does not suck back.) Disconnect the reaction tube and place it in an inclined position to displace the gas in it with air, or aspirate air through it for a minute or two. When cool, weigh it. Transfer the gas tube to a deep cylinder of water and read its volume.

Iron "reduced by hydrogen" may be used in place of the nails, but it should be heated (and cooled) in the tube in a current of hydrogen just before the experiment, and must be held in place in the tube by wads of asbestos.

Calculation. Find the normal volume and the weight of the hydrogen, and determine the equivalent of chlorine, the percentage composition of hydrogen chloride, and its formula.

The relative volumes of hydrogen chloride, hydrogen, and chlorine may also be found from the data of this experiment, for the weight of the hydrogen chloride which was analysed equals the sum of the weights of the hydrogen and chlorine, and these weights divided by the weights of 1 cc. of the respective gases will give the ratios by volume.

Example. Chlorine (gain of iron) = 517.00 mg.
Wt. of hydrogen = 14.54

Wt. of hydrogen chloride = 531.54

Equivalent of chlorine (hydrogen = 1), $517 \div 14.54 = 35.56$; percentage composition,—chlorine = 97.26 %, hydrogen = 2.74 %; formula,—

$$517 \div 35.45 = 14.58 \text{ and } 14.54 \div 1 = 14.54;$$

hence the formula is HCl (confirmed by a density determination). Volumetric relations: dividing each weight by the weight of 1 cc. of the gas, $531.54 \div 1.63 = 326.1$, $517 \div 3.16 = 163.6$, and $14.54 \div 0.09 = 161.6$, the volumes are found to be (nearly) in the proportion of one each of chlorine and hydrogen to two of hydrogen chloride, and the volumetric equation is:

$$H_2 + Cl_2 = 2HCl.$$

12. **Volumetric Composition of Hydrogen Chloride.** Hydrogen chloride which fills a flask of known volume is dissolved in water, and its hydrogen is set free by magnesium and measured.

Apparatus. A 400 to 500 cc. round-bottomed flask fitted with stopper and tubes as in Fig. 10 (p. 33) and a hydrogen chloride generator.

1. *Experiment.* Put from 220 to 280 mg. of magnesium ribbon (calculate the amount required for the flask full of hydrogen chloride and use a little more) into the perfectly dried flask, and fill the flask with dry hydrogen chloride as in 6, 5 (p. 35). When the air is completely displaced, disconnect and close the flask with screw pinch-cocks or glass plugs. Now bring the neck of the flask under water and open the shorter tube. If the water does not enter, pour cold water on the flask. After 50 to 100 cc. of water have entered, close the tube, and keeping the neck of the flask under water to prevent leakage of air into the partial vacuum, rinse the walls of the flask with the water it contains. Leave it with the water seal till the evolution of gas has stopped. Then open the short tube and allow water to enter until, with the same level of water within and without, no further movement occurs; close the tube for a moment and place the flask upright. Measure the liquid and determine the total capacity of the flask with stopper in place as in 6 (p. 32).

2. A variation of this method may be carried out in which the hydrogen is collected in a gas tube over water. Fill the flask (of not more than 400 cc. capacity if a 200 cc. gas tube is used) with hydrogen chloride as before, but without putting in the magnesium. After dissolving the gas in a little water, place the flask upright and connect it with a delivery tube whose end is under the filled and inverted gas tube. Drop into the flask about 200 mg. of magnesium ribbon and quickly insert the stopper. When the evolution of gas has entirely ceased, measure the capacity of the flask, and the collected hydrogen, and make the same corrections as in the last experiment.

Remarks. The smaller the amount of water which is introduced to dissolve the hydrogen chloride, the more rapid will be the evolution of the hydrogen. The action on the metal becomes very slow towards the last, and it may be necessary to wait over night for its completion. It is, therefore, best to take barometer and temperature readings at the time of filling with hydrogen chloride, and again when measuring the hydrogen, so that any necessary corrections may be made. Further, as the hydrogen chloride is dry, and the hydrogen is saturated with moisture, the volume of the latter should be corrected for aqueous tension (*cf.* p. 28).

Compare the corrected volume of hydrogen with that of the hydrogen chloride.

13. **Analysis of Ammonia.** Ammonia is decomposed by heated copper oxide and the nitrogen collected; from this and the loss in weight of the copper oxide the composition of ammonia is determined.

Apparatus as shown in Fig. 14, and a 200 cc. gas tube. The U tube is filled with fragments of fused potassium hydroxide, or of quick-lime.

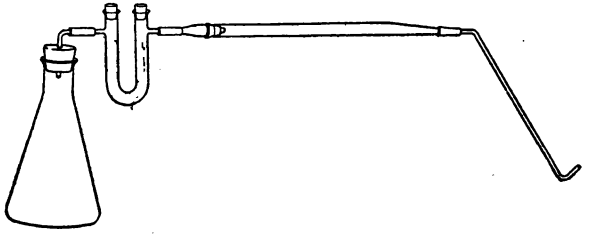

FIG. 14.

Experiment. Place a loose wad of asbestos in the reaction tube 5 cm. from its small end, and then

introduce enough finely granulated copper oxide to occupy about 6 cm. of its length and a second wad of asbestos to hold the oxide in place. Dry the copper oxide by heating it for a few minutes in a current of air, and when it is cool weigh the tube and its contents.

Put about 100 cc. of concentrated ammonia solution in the flask, connect the apparatus and arrange the gas tube for collecting the nitrogen over water. Drive a rapid current of ammonia through the apparatus till all the gas is absorbed in water at the end of the delivery tube. Now bring the delivery tube under the gas tube and heat the copper oxide. When about 160 cc. of gas have collected, stop heating, but continue the current of ammonia till absorption is again complete. (Be careful that the water does not suck back into the reaction tube.) When the tube is cool, disconnect it, dry its smaller end, if necessary, with rolls of filter paper, place it vertically for a short time (or aspirate air through it) to displace the ammonia with air, and weigh. Read the volume of nitrogen with the usual precautions.

Calculation. The loss of weight of the reaction tube represents the weight of oxygen which has united with the hydrogen of the ammonia whose nitrogen has been collected. The weight of the hydrogen is very nearly one eighth of this loss. The weight of the nitrogen is found from its volume in the usual way. Find the equivalent of nitrogen; the percentage composition of ammonia, and its formula.

Example. Loss of oxide ÷ 8 (= hydrogen) = 40.6 mg.
Weight of nitrogen = 188.4

Weight of ammonia analyzed = 229.0

Calculations made as in the case of hydrogen chloride (page 47), give: equivalent of N = 4.67; percentage composition of ammonia,—nitrogen = 82.37 %, hydrogen = 17.73 %; empirical formula, NH_3; volumetric relations,—ammonia 2, hydrogen 3, nitrogen 1.

14. **Volumetric Analysis of Ammonia by Chlorine.** A known volume of chlorine is brought in contact with an excess of ammonia and the volume of nitrogen set free is measured.

Apparatus. A 200 cc. gas tube or a larger flask; a chlorine generator with wash bottles of water and concentrated sulphuric acid; a glass tube long enough to reach to the bottom of the gas tube or flask.

Experiment. Fill the gas tube (or flask) with dry chlorine (under the hood), placing the tube with its open end up and leading the chlorine to the bottom of it through the long glass tube. When sure that it is full, withdraw the latter slowly while the current of gas continues, immediately close the gas tube with the thumb or a rubber pad, and invert it in a dish of concentrated ammonia. After the absorption has ceased, close the tube and transfer it to a dish of water standing in a sink. Attach a long rubber tube to the faucet and turn on the water. When the air is all displaced from this tube, bring its end into the gas tube, pushing it up into the space occupied by the gas, and continue the stream of water till the ammonia is all washed out of the tube and the dish. (This is necessary as the tension of the ammonia gas from the solution influences the volume of the nitrogen, and the ammonia would be removed very slowly by diffusion.) Now transfer the gas tube to the deep vessel for reading, and note the volume with the

usual precautions. Find the total capacity of the gas tube by water measure.

Calculation. Since the chlorine was dry and the nitrogen moist, the volume of the latter should be corrected for aqueous tension (*cf.* p. 28). Any considerable difference in temperature between the chlorine and the nitrogen should also be taken into account. The barometer is not likely to change enough during the experiment to make a pressure correction necessary.

The experiment gives the relation of the volume of nitrogen to that of the chlorine which sets it free from hydrogen in ammonia. But since chlorine and hydrogen are known to combine in equal volumes, we may infer that the volumetric ratio of nitrogen and hydrogen in ammonia is that of the nitrogen and chlorine found in the experiment.

Write a molecular (volumetric) equation showing the analysis of ammonia into its constituents.

15. Volumetric Analysis of Ammonia by Sodium Hypobromite. A known volume of ammonia is brought in contact with a solution of sodium hypobromite, and the nitrogen liberated is measured.

Apparatus. A gas tube fitted with stopper and tubes as in Fig. 10, p. 33; an ammonia generator with a potassium hydroxide drying tube.

Experiment. Prepare enough strong sodium hydroxide solution to fill the gas tube, and add to it a few cc. of bromine. Fill the tube with ammonia as for a density determination (p. 35), and open the shorter tube under the hypobromite solution. (The liquid may be made to enter by pouring cold water on the

tube.) After the action has stopped, close the tube and transfer it to a deep cylinder of water. When the heavy solution has disappeared from the tube, adjust the water levels and read the volume. Finally find the total capacity of the tube with stopper in place (*cf.* p. 32).

Calculation. As the ammonia was dry, and the nitrogen measured over water, a correction should be made for this (*cf.* p. 28), and also for any difference in temperature between the gases. The relation between the volumes of ammonia and nitrogen should be compared with the volume relations of hydrogen and nitrogen determined in the last experiment.

16. **Analysis of Hydrogen Sulphide.** Hydrogen sulphide is led over heated iron or copper, and the hydrogen collected.

Apparatus. A reaction tube; a 200 cc. gas tube; a delivery tube; a generator for making hydrogen sulphide from antimony sulphide and hydrochloric acid, with a water wash bottle and a calcium chloride drying tube.

Experiment. Fill the gas tube with strong sodium hydroxide solution and invert it in a dish of the solution (use the rubber pad). Put several grams of iron "reduced by hydrogen" and dried by heating in a current of hydrogen, or of copper foil, in the reaction tube, and weigh it. Lead the gas, washed with water and dried with calcium chloride, through the reaction tube, and test for displacement of air from the apparatus by collecting from time to time a few of the bubbles from the delivery tube in a test tube filled with the sodium hydroxide solution. After the absorption is complete, bring the delivery tube under

the gas tube and heat the metal. The action is rather slow. When about 180 cc. of gas have been collected, remove the burner, but continue the current of gas for a few minutes to flush the hydrogen from the tubes. Let the gas tube stand for a short time to completely absorb any hydrogen sulphide, and then transfer to the reading cylinder, and measure the gas as usual. Weigh the reaction tube after it is cool and the hydrogen sulphide has been replaced with air by aspiration.

Calculation. The weight of the hydrogen is calculated, and the difference in the weights of the reaction tube gives the weight of sulphur which was combined with it. These data may be used to determine the equivalent of sulphur, or the percentage composition of hydrogen sulphide, and its formula as in the case of hydrogen chloride (p. 47).

Example. The hydrogen collected measured 192 cc. at 760 mm. and 18°; its normal volume was calculated to be 180.1 cc. and its weight (180.1 × 0.09) 16.21 mg.

Weight of sulphur (gain of iron)	= 257.00 mg.
Weight of hydrogen	= 16.21
Weight of hydrogen sulphide	273.21

Equivalent of sulphur = 15.85; composition of hydrogen sulphide, sulphur = 94.07 %, hydrogen = 6.93 %; formula H_2S; volume relations of hydrogen and hydrogen sulphide, 1 : 1.

17. **Synthesis of Sulphur Dioxide.** A weighed amount of sulphur is burned in a current of air and the sulphur dioxide absorbed in potassium hydroxide solution, whose increase in weight is determined.

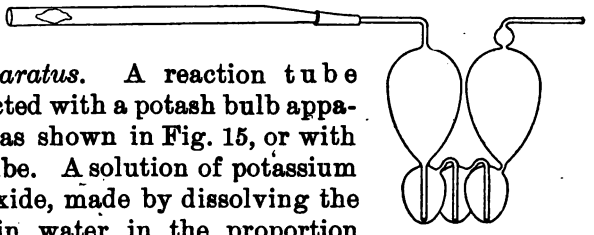

FIG. 15.

Apparatus. A reaction tube connected with a potash bulb apparatus as shown in Fig. 15, or with a U tube. A solution of potassium hydroxide, made by dissolving the solid in water in the proportion of one to two, about half fills the three lower bulbs, or just closes the bend of the U tube. This absorption apparatus should be closed by short rubber tubes and glass plugs when not in use.

Experiment. Place a loose wad of asbestos near the small end of the reaction tube and weigh the tube with about 400 mg. of roll sulphur. Weigh the absorption apparatus, and connect it with the reaction tube, and with an aspirator by rubber tubing bearing a screw pinch-cock. Put the sulphur about 3 cm. from the end of the tube, and start the current of air, regulating it so that it passes through the solution at the rate of 4 to 5 bubbles a second. Now heat the sulphur till it ignites. (The tube must be quite level to prevent the melted sulphur from flowing either way.) At the end of 15 or 20 minutes check the air so that the sulphur stops burning, and then let it flow again at the former rate for 3 or 4 minutes to draw all the gas into the solution. Weigh the reaction tube with the sulphur which remains in it, and the absorption apparatus.

More accurate results may be expected, if a very small drying tube filled with solid potassium hydroxide is connected with the potash bulbs to absorb any gas and water vapor which may escape from the solu-

tion; and if the air enters the reaction tube through a U tube similarly loaded. The first tube forms part of the absorption apparatus and is weighed with the potash bulbs.

Use the results as in 11 (p. 47).

Example.	Sulphur dioxide	= 220 mg.
	Sulphur burned	= 109
	Oxygen	= 111

Equivalent of sulphur is 7.86; the percentage composition of sulphur dioxide is S = 49.55% and O = 50.45%; the formula is SO_2; and the volume relations of oxygen and sulphur dioxide are 1 : 1.

18. Analysis of Carbon Dioxide. Carbon dioxide is led over heated zinc dust and the carbon monoxide collected over water.

Apparatus. A reaction tube; a 200 cc. gas tube and a delivery tube; a carbon dioxide generator with water wash bottle and calcium chloride drying tube.

Experiment. Place a loose wad of asbestos near the small end of the tube and then add a few grams of zinc dust, which should not more than half fill the section of the tube and is held in position by another wad of asbestos. Dry the zinc dust by heating gently in a current of air, and when cool weigh the tube, and connect it with the source of dry carbon dioxide. Arrange for the collection of the carbon monoxide over sodium hydroxide solution as for the hydrogen in the analysis of hydrogen sulphide (p. 53), make the same test for the displacement of the air, and proceed further as in that experiment. The current of carbon dioxide should be at the rate of 2 or 3 bub-

bles a second in the wash bottle. Make calculations similar to those in 11 (p. 47).

A synthesis of carbon dioxide from carbon and oxygen, while an apparently easy experiment, cannot be recommended; since the results are not likely to be satisfactory without greater precautions than are suited to these simple exercises. The quantitative composition of carbon dioxide may, however, be inferred from the results of the last experiment and determinations of the densities of the two oxides of carbon.

VIII

THE HYDROGEN EQUIVALENT OF METALS

The equivalent or combining weight of some metals as compared with hydrogen may be found by determining how much hydrogen is displaced from an acid or water by a known weight of metal.

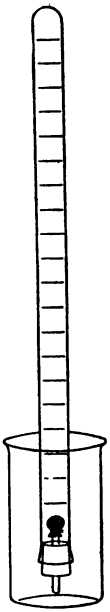

FIG. 16.

19. **Determination of the Hydrogen Equivalent of Metals.** *First Method.* The apparatus is shown in Fig. 16. The small tube projects about 3 cm. into the gas tube, and is capped loosely with a thin piece of muslin tied to it with thread. This prevents loss of fragments of metal and of gas bubbles which otherwise might be swept out of the tube by the current of liquid displaced by gas.

Experiment. Fill the gas tube with acid and water as directed in each case, pouring in the water slowly down the wall of the tube, at first, so that it shall mix with the acid as little as possible. Drop in the weighed metal, immediately insert the stopper, and, closing the end of the small tube with the finger, bring it into a beaker containing a little water. As the metal must pass through water before reaching the acid, there should be no loss of gas. Be careful not to enclose a bubble of air when inserting the stopper.

As the action proceeds, wash down any particles of metal which adhere to the walls by inclining the tube. When the metal has all disappeared, transfer the tube to a deep cylinder, remove the stopper under water, and read the volume with the usual precautions.

Second Method. The apparatus is indicated in Fig. 17. The flask is of 100 cc. capacity. A glass rod which fits in the stopper gas-tight, with the aid of a film of grease, is enlarged at one end by softening in the flame and pressing on an asbestos pad. To this end is fastened a platinum wire attached to a tray of platinum foil (copper may be used) small enough to enter the mouth of the flask freely.

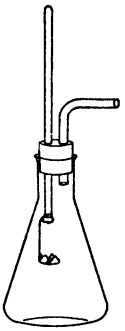

FIG. 17.

Experiment. Charge the flask with acid as directed in each case, and adjust the tray so that it is above the acid when the stopper is inserted. Put the weighed metal on the tray, insert the stopper, connect a delivery tube, and arrange for the collection of the hydrogen over water, placing the flask in a dish of water of room temperature; then lower the tray into the acid. When the metal is all dissolved, read the volume of gas as usual.

Calculation. The hydrogen is reduced to normal volume and its weight calculated. This weight divided into the weight of the metal used gives the equivalent of the metal with hydrogen = 1.

The weights of the metals given in the following directions are those which should be taken when a 200 cc. gas tube is used.

1. *Aluminium.* Weigh about 140 mg. of aluminium wire or sheet. Pour 40 cc. concentrated hydrochloric acid into the gas tube and fill it up with water; or use about 50 cc. of acid, 1 : 5, in the flask.

2. *Calcium.* Take about 310 mg. of the brightened metal (*cf.* p. 104, note). If the first method is used, cover the surface of the weighed metal with a slight film of oil; this delays the reaction so that the stopper can be inserted without danger of losing hydrogen. Put 2 cc. of hydrochloric acid in the gas tube and fill it with water; or use in the flask 50 cc. of water with 1 cc. of the acid.

3. *Magnesium.* Take about 190 mg. of magnesium ribbon. Use in the gas tube 40 cc. of sulphuric acid, 1 : 4, or 10 cc. of concentrated hydrochloric acid; in the flask, 50 cc. of either acid, 1 : 20.

4. *Zinc.* Weigh about 510 mg. of pure zinc, and wind the metal with a piece of fine platinum wire. Put in the gas tube 50 cc. of sulphuric acid, 1 : 4, or of concentrated hydrochloric acid; or use in the flask 50 cc. of sulphuric acid, 1 : 12, or of hydrochloric acid, 1 : 4.

Third Method. With cadmium, iron, and tin, heat is necessary, and the experiment is conducted as follows: Fit a 30 or 40 cc. test tube with a rubber stopper and gas delivery tube whose end projects about 1.5 cm. into the test tube. Arrange a clamp to support the test tube for heating, and a gas tube for collecting the hydrogen over water. Fill the test tube with acid as directed, drop in the metal, and insert the stopper. The acid will be forced into the delivery tube, partly filling it. Place the test tube in the clamp and heat gently. As soon as the air is all

driven out of the delivery tube, bring its end under the gas tube. Heat sufficiently to keep up a brisk evolution of gas, and when the metal has disappeared, boil the solution till no more gas is delivered.

A piece of fine platinum wire should be wound on the metal to aid the reaction.

5. *Cadmium.* Take about 875 mg., and use concentrated hydrochloric acid.

6. *Iron.* Take about 435 mg. of pure iron wire, and use hydrochloric acid, 1 : 1.

7. *Tin.* Take about 915 mg. of granulated tin or pure tin foil, and use concentrated hydrochloric acid.

8. *Sodium.* Seal one end of a glass tube of about 5 mm. inside diameter, cut it off to a length of 3 or 4 cm. and weigh it. With a glass rod or stout wire ram into it tightly under kerosene about 360 mg. of sodium. Wipe it dry and weigh it. To prevent the water from entering at once, stuff a wad of cotton into it. Bring the open end under the mouth of a gas tube which has been filled and inverted over water, and remove the cotton with pincers. If the water does not enter, use a wire to aid it. (A lead tube hammered together at one end may be used instead of the glass tube, but its weight and opacity are both disadvantages.) If the sodium is not welded into a compact mass in filling the tube, bits of it may become detached and the action grow too violent.

Example. Iron wire = 417 mg.; hydrogen = 186 cc., at 20° and 754.5 (cor.). Normal volume = 168 cc.; weight of hydrogen = 15.1 mg.; hydrogen equivalent of iron = 27.6.

IX

OXIDES AND SULPHIDES OF THE METALS

I Oxides

The composition of the oxides of metals may be determined by synthesis or analysis; but in no case is a direct synthesis entirely satisfactory. The conversion of magnesium into oxide by burning it in air is often given as a quantitative experiment, but cannot be recommended. If, as usually directed, the magnesium is burned in a porcelain crucible whose cover is lifted from time to time to admit air, there is always some visible loss; after this danger is past, it is difficult to completely oxidize all of the remaining metal. Magnesium unites with nitrogen as well as with oxygen, and some nitride is almost always formed, as can be proved by the odor of ammonia when the residue is moistened with water. Further, the porcelain is attacked with the production of a black stain,—a reaction which the student usually cannot account for. The loss of oxide may be prevented if the magnesium is burned in a glass tube in a current of air, but the other difficulties remain.

Finely divided copper can be quantitatively oxidized by heating a current of air, but the results are not as satisfactory as those obtained by a reduction of the oxide.

Though the complete conversion of metals into their oxides by direct synthesis is difficult, many oxides may be made quantitatively from the metals in an indirect way; and the composition of a considerable number can be determined by reduction of the oxides by heat alone, or by heating in hydrogen or with charcoal. Some oxides may also be produced quantitatively from salts of metals. The results of the determinations may be used to find the equivalents of the metals; of acid groups, assuming the equivalents of the metals as known; the percentage composition of the oxides; and the formulas, assuming the atomic weights as known.

20. **Indirect Synthesis of Oxides of Metals.** The experiments are carried out in porcelain crucibles of 60 cc. capacity. The general procedure is the following: Weigh in the crucible a suitable amount of the metal. Add a few cc. of distilled water and then concentrated nitric acid. Avoid an unnecessary excess of acid. (Each cubic centimeter contains nearly 1 g. of pure acid.) Heat nearly to boiling after the first addition and then add a few drops at a time till the metal is all dissolved. Keep the crucible covered with a watch-glass, and hasten the action, if necessary, by a gentle heat, preferably on a water bath. When the metal has all disappeared, rinse the cover-glass into the crucible, and evaporate the solution on the water bath or over a very low flame under the hood. Now heat the crucible on a pipe-stem triangle very cautiously with a low flame protected by a chimney, as long as any fumes are given off, and then strongly for a few minutes. When the crucible is cool, weigh it, and repeat the final heating, cooling, and weighing. Calculate in each case the ratio of the

metal to oxygen = 8, the percentage composition of the oxide, and its formula.

The metals whose oxides can be quantitatively formed in this way are the following: *Antimony, bismuth, cadmium, cobalt, copper, iron, lead, magnesium, mercury, nickel, tin,* and *zinc.* Suitable weights for the determinations are about 2 grams of lead or mercury, 0.5 gram of magnesium, and 1 gram of each of the other metals.

In a few cases the conduct of the experiment requires certain additional directions. *Antimony* and *tin* should be treated with strong nitric acid. They do not dissolve, but form solid compounds; and care must be taken that no particles of the metal remain hidden in the white product. *Cadmium* and *magnesium nitrates* require special care in the final heating. *Copper nitrate* cannot be changed into oxide without loss when heated by itself; but if some solid oxalic acid is added to the residue from evaporation, the loss is prevented. *Iron* should be used in the form of pure wire. *Mercury nitrate* must be heated carefully, avoiding a high temperature, and constantly stirred with a short glass rod. It is difficult to convert all of the nitrate into oxide without decomposing some of the latter. The stirring rod must be thoroughly cleaned into the crucible before the final weighing. In the decomposition of *lead nitrate*, avoid melting the oxide by too high a temperature. *Calcium* reacts with the water first added; when this action is over, add dilute nitric acid, drop by drop, till all is dissolved, then evaporate, and ignite; or, the hydroxide and the oxide may both be determined as follows: Add water to the weighed calcium in the crucible, evaporate, and heat with a very low flame,

placing the crucible in another of the same size. When the weight is constant, use the result as hydroxide. Now heat the hydroxide strongly, and weigh the product as oxide. The oxide may be converted back into the hydroxide by moistening with water and heating cautiously as before. *Aluminium* can be made into oxide by dissolving it in hydrochloric acid, evaporating, and heating with the addition of solid oxalic acid.

Example. 1.013 g. of iron gave 1.446 g. of oxide; hence the ratio of iron to oxygen = 8 is 18.72; the percentage composition, iron = 70.06 % and oxygen = 29.94 %; and the formula is Fe_2O_3, for 70.06 ÷ 55.9 = 1.25, and 29.94 ÷ 16 = 1.87; and 1.25 : 1.87 : : 2 : 3 (nearly).

21. **Analysis of Oxides of Metals by Heat.** The analysis of *mercuric oxide* has already been described (p. 29). *Silver oxide* is reduced to silver, and the *higher oxides of lead* to lead monoxide by heating in a porcelain crucible.

The *oxides of lead* must be thoroughly dried before the experiments by standing for some days over concentrated sulphuric acid in a desiccator. Take about 2 grams of each, and heat in the crucible, stirring occasionally with a short glass rod, and taking care that the monoxide does not melt. When the change seems to be complete, let the crucible cool, and weigh. Repeat the heating to constant weight.

The *silver oxide* for the experiment is prepared as follows: Precipitate the oxide from a solution of silver nitrate by a solution of barium hydroxide or of sodium hydroxide. Wash the precipitate, as soon as it has subsided, with water many times by decantation, bring it on to a filter paper to remove most of the

water, and then heat it in a dish on the water bath until it seems dry. Finally, let it stand in a desiccator over sulphuric acid for a day or two. Take about 0.5 gram for the determination. It is not necessary to repeat the heating.

Example. 543 mg. of silver oxide gave 505 mg. of silver; hence the equivalent of silver is 106.3; the percentage composition is silver = 93 %, and oxygen = 7 %; the formula Ag_2O, for $93 \div 107.93 = 0.862$, and $7 \div 16 = 0.437$,—and $0.862 : 0.437 :: 2 : 1$ (nearly).

22. **Analysis of Oxides of Metals by Hydrogen.** The procedure is the same as in the case of copper oxide (p. 44), except that the weighed calcium chloride tube is omitted, unless it is desired to determine the oxygen (by weighing the water it forms) as well as the metal. The oxides which may be quantitatively reduced to metals in this way are: the oxides of *bismuth*, *cadmium*, *cobalt*, *copper* (cuprous and cupric), *iron*, *lead* (all the oxides), *nickel*, *silver*, and *tin*. *Manganese dioxide* and the *red oxide*, Mn_3O_4, are reduced to manganous oxide, MnO. The oxides made in the experiments under 20 may be used. All of the oxides must be thoroughly dried before weighing them for the experiments.

Experiments. Weigh the reaction tube with a wad of freshly ignited asbestos placed about 6 cm. from its narrow end, introduce about one gram of the dry oxide, and weigh again. Connect the tube with a source of dry hydrogen, and, after the air is all driven out, begin heating the oxide. When the reduction appears complete, let the tube cool in the current of hydrogen, disconnect it, and empty it of hydrogen, before weighing, by holding it vertically for a minute or two.

Cobalt, *nickel*, and *tin* require a rather high temperature; *iron* is reduced at a low temperature, but should be heated strongly at the end of the reduction, else it may re-oxidize on exposure to air; *cadmium* volatilizes somewhat, forming a metallic mirror. *Lead peroxide* ignites almost explosively at first, and it is better, in studying the lead oxides, to reduce the higher oxides to the monoxide by heat alone, and then determine the composition of the monoxide by reduction in hydrogen. The reduction of *lead monoxide* does not require a high temperature, and care must be taken not to melt the oxide in the reduction tube. *Lead* and *bismuth* give metallic globules.

Red manganese oxide may be prepared for the experiment by heating the carbonate in a Bunsen flame, or the sulphate with the blast lamp.

Example. 1.010 g. of tin oxide gave 0.798 g. of tin; hence, the ratio of tin to oxygen = 8 is 30.11; the percentage composition, tin = 79.01 %, and oxygen = 20.99 %; the formula is SnO_2, for 79.01 ÷ 119 = 0.664, and 20.99 ÷ 16 = 1.312; and 0.664 : 1.312 : : 1 : 2 (nearly).

23. Analysis of Arsenic Trioxide. Weigh about 500 mg. of vitreous arsenic trioxide, and put it in an unweighed ignition tube about 20 cm. long. Add a layer of sharply dried sugar charcoal about 5 cm. high, and partly close the tube with an adapter drawn out to a small tip. Heat the charcoal first to a high temperature without heating the arsenic oxide, and then slowly volatilize the oxide into the hot charcoal. When the oxide has all disappeared, allow the tube to cool, and cut it off below the arsenic mirror. Wipe out any moisture with filter paper, and weigh. Then dissolve the arsenic with dilute nitric acid in a test tube, wash, and dry the tube, and weigh it.

Example. From 542 mg. of arsenic trioxide were obtained 410 mg. of arsenic. Arsenic in the trioxide, 75.65 %; equivalent of arsenic, 24.84; formula of the oxide, As_2O_3.

24. Oxides of Metals from Salts. Determinations may be made of several oxides from salts of the metals. A few such experiments are given below. Their results may be employed to ascertain the equivalents of the acid groups.

Experiments. Powder and dry the salt. Weigh in a porcelain crucible about 2 g., except in the case of the ammonium dichromate, and heat as directed, repeating to constant weight.

1. *Lead oxide from the nitrate.* Dry by heating a little above 100°. Heat to decomposition and constant weight, but avoid melting the oxide.

2. *Copper, manganese, and iron oxides from the sulphates.* Take either the crystallized salts of copper and manganese, or their anhydrous salts after determining the "water of crystallization" (p. 92). Use ferrous ammonium sulphate for the iron oxide experiment. Dry the crystallized salts by pressing them between the folds of filter paper. Mix with two or three times the bulk of solid ammonium carbonate, and heat to the highest temperature possible with the Bunsen burner, or in the flame of a blast lamp. Repeat with addition of ammonium carbonate, if necessary. The manganese oxide is Mn_3O_4.

3. *Calcium and manganese oxides from the carbonates.* *a.* Use finely powdered calcite for the calcium carbonate. Heat it strongly (best with a blast lamp) for twenty minutes; cool, and weigh, and then repeat the heating, cooling, and weighing, for five minutes at

a time, to constant weight. *b*. Dry the manganese carbonate over sulphuric acid, and heat by a Bunsen burner till of a uniform color. The oxide is Mn_3O_4.

4. *Chromium oxide from ammonium dichromate.* Weigh about 0.5 g., cover the crucible, and, holding the cover down with the crucible tongs, heat gently till the reaction begins, and then withdraw the burner. When the reaction seems to be over, heat strongly for a few minutes. Dust off the cover into the crucible, cool, and weigh.

Conversion of Oxides of Metals into Salts. Some oxides may be quantitatively changed into salts of the metals: oxides of cadmium, calcium, lead, and zinc into chlorides, and calcium oxide into fluoride (p. 74); oxides of lead and silver into nitrates (p. 79); oxides of calcium, chromium, iron, nickel, and zinc into sulphates (p. 86).

II Sulphides

25. **Synthesis of Sulphides of Metals.** Only a few sulphides can be made quantitatively by the direct union of the metals with sulphur. *Copper*, *iron*, *nickel*, and *silver* may be converted into sulphides by heating with sulphur in a covered porcelain crucible.

Experiments. Weigh about 1 gram of the metal in a porcelain crucible, add about an equal amount of sulphur, cover the crucible, and heat strongly till no more flames of burning sulphur are seen under the edge of the cover. Allow the crucible to cool with the cover on. If on examination it is found that all the sulphur has not disappeared from the crucible, heat again for a few minutes. Weigh the crucible and its contents, when cool, without the cover.

Copper is used in the form of foil or thin sheet; *iron* and *nickel*, in the finely divided state obtained by

reduction of their oxides in hydrogen; *silver*, in the form of foil, or as produced by the reduction of the chloride by zinc, or of the nitrate by heating with charcoal (*cf.* p. 80). In the cases of the powdered iron and nickel, the heating should at first be cautious to avoid loss through the violent boiling of the sulphur.

26. Reduction of Sulphides of Metals. By heating in hydrogen, the higher sulphides of *copper*, *iron*, and *tin* may be reduced to lower sulphides. For these experiments use finely powdered pyrites, stannic sulphide, and cupric sulphide. The last two may be prepared by precipitation from stannic chloride and copper sulphate solutions, washing thoroughly by decantation with water containing hydrogen sulphide, draining on a filter, drying on a water bath and finally over sulphuric acid in a desiccator.

The experiments are conducted in the same way as in the reduction of oxides by hydrogen (*cf.* p. 66).

27. The Sulphide of a Metal from the Oxide. An experiment, whose results may be used to find the ratio of sulphur to oxygen, is the conversion of *cadmium oxide* into sulphide. The cadmium oxide used may be that made from the metal (p. 64). Weigh about one gram in a crucible, add about an equal weight of sulphur, cover the crucible, and heat till the sulphur flames have disappeared. Do not remove the cover till the crucible is cool. The change is usually complete the first time, but the addition of sulphur, and heating should be repeated, if necessary, to constant weight.

Example. From 1.086 g. of cadmium oxide, 1.221 g. of cadmium sulphide was obtained. From a synthesis of cadmium oxide (p. 64), the cadmium in the

oxide was found to be 87.72 %. Hence the weight of cadmium in the oxide taken for the experiment, and also in the sulphide produced, was 0.953 g.; subtracting this from the experimental weights, the weight of oxygen is 0.133 g., and that of sulphur 0.268 g., whence the ratio of oxygen to sulphur is 1 : 2 (nearly); the equivalent of sulphur, 16.12.

28. Sulphides of Metals from Sulphates. 1. *Barium sulphate* is reduced to the sulphide in hydrogen. Weigh about 1 g. of the dry salt, and proceed as in the reduction of oxides by hydrogen (p. 66), heating strongly, and repeating to constant weight.

2. *Lead* and *zinc sulphates* are converted into sulphides by heating with sulphur. Weigh about 1 g. of the dry lead sulphate, or of anhydrous zinc sulphate (the water of crystallization may be determined as a preliminary exercise, *cf.* p. 92), add sulphur, and heat sharply in a covered crucible, repeating, with fresh additions of sulphur, to constant weight. Three or four repetitions will probably be necessary.

Lead and zinc sulphides may be converted into sulphates (*cf.* p. 86).

X

THE HALIDES OF THE METALS

The halides of metals can be made quantitatively from metals, from oxides or sulphides, and from salts, by treatment with hydrochloric acid. The data of the experiments may be used to find the equivalents of the halides (assuming a knowledge of the equivalents of the metals, or of the composition of the oxides, sulphides, and salts employed, and the equivalents of the metals or acid groups); or to find the equivalents of acid groups (if those of the metals or halides are known). The percentage composition of the halides should be reckoned, and the formulas derived (assuming the atomic weights).

29. **Synthesis of Halides of Metals.** The composition of halide compounds of the following metals may be determined by synthesis from the metal: *Cadmium*, *calcium*, *copper*, *lead*, *silver*, *sodium*, and *zinc*.

Experiments. 1. *Zinc Chloride.* Weigh about one gram of zinc, and dissolve it in hydrochloric acid in a weighed conical flask of 100 cc. capacity. Avoid using an unnecessary excess of acid (each cubic centimeter of the concentrated acid contains about 460 mg. of HCl). When the metal is dissolved, evaporate over a low flame or on a sand bath, and heat, at the last, until the substance is just fused. Zinc chloride is hygroscopic, and the flask should, therefore, be

closed with a cork if it stands for any time before the final weighing.

2. *Calcium Chloride.* Bring into a weighed crucible from 0.5 to 1 gram of calcium, add a little water and cover with a watch-glass. When the action has ceased, rinse the watch-glass into the crucible, and add hydrochloric acid, drop by drop, till in slight excess. Add a little ammonium chloride, evaporate, and heat till no more vapors are given off. Cool and weigh as soon as possible, or keep the crucible in a desiccator until it can be weighed.

Calcium fluoride may also be made from calcium in the same way, using hydrofluoric acid and a platinum crucible.

3. *Sodium.* Weigh from 0.5 to 1 gram of sodium in a tube as described on page 61, bring it into a weighed crucible about two-thirds full of water, and cover the crucible with a watch-glass. When the sodium has disappeared, rinse the watch-glass into the crucible, and, leaving in the crucible the tube in which the sodium was weighed, add hydrochloric acid to acid reaction. Evaporate to dryness and heat till no more acid odor is perceived. Subtract from the final weight the sum of the weights of the crucible and the tube.

4. *Cadmium, Copper, and Lead Chlorides.* Weigh in a crucible about one gram of the metal, add a little water, and then concentrated nitric acid, a little at a time (*cf.* p. 63), till the metal is all dissolved. (Cover with a watch-glass.) Now add about 3 cc. of concentrated hydrochloric acid, evaporate on a water bath, and then heat over a low flame or on a sand bath till no more vapors appear. Cool and weigh.

5. *Silver Halides.* *a.* Dissolve the metal in nitric acid as in the last experiment. Add hydrochloric acid or ammonium bromide or iodide (in solution), taking care that the precipitation is complete, and avoiding unnecessary excess; evaporate, and heat till the halide just begins to melt.

b. Convert the silver into nitrate as before, but in an unweighed beaker. Add water to half fill the beaker, heat nearly to boiling, and precipitate with hydrochloric acid or a solution of potassium bromide or iodide. When completely precipitated, allow the halide to settle, wash it thoroughly by decantation with distilled water, and dry it in the beaker on a water bath. Now transfer it to a weighed crucible by aid of a brush, and heat as before. The precipitation and washing may be carried out in a weighed crucible, but it is better to use the beaker.

30. Halides of Metals from Oxides. 1 *The chlorides of cadmium, calcium, lead,* and *zinc* may be made from the oxides of these metals by treatment with hydrochloric acid. Dry the oxides by heating, weigh about one gram in a porcelain crucible, add a little concentrated hydrochloric acid, and heat (under the hood) over a low flame to constant weight (*cf.* **29**, 1, 2 and 4, pp. 72 and 73).

Calcium fluoride may also be made from calcium oxide. Use a platinum crucible and hydrofluoric acid.

2. *Silver Iodide* may be made by heating silver oxide with iodine. Weigh about 0.5 g. of the oxide (*cf.* p. 65 for its preparation) in a porcelain crucible, add a little iodine, cover, and heat with a low flame until the reaction takes place, then remove the cover, and slowly volatilize the excess of iodine. Finally, heat till the iodide begins to melt.

Example. From 613 mg. of silver oxide 1238 mg. of silver iodide were obtained. An analysis of silver oxide (p. 65) shows that it contains 93.11 % of silver; therefore the weight of silver in the oxide used was $613 \times .9311 = 570.8$ mg. Subtracting this from the weights of the oxide and of the iodide, we find the weights of oxygen and of iodine which are equivalent, $613 - 570.8 = 42.2$ mg. of oxygen, and $1238 - 570.8 = 667.2$ mg. of iodine. The equivalent of iodine is, therefore, $(667.2 \times 8) \div 42.2 = 126.48$.

31. **The Chloride of a Metal from its Sulphide.** 1. *Zinc Chloride* can be made quantitatively from the sulphide. The zinc sulphide for the experiment may be that made from the sulphate (p. 71). If the purchased sulphide is used, it should be sharply heated with sulphur in a covered crucible till the excess of sulphur is driven off, and allowed to cool before removing the cover. Weigh about one gram of the sulphide in a 100 cc. conical flask, add concentrated hydrochloric acid, and proceed as in making the chloride from the metal (p. 72).

2. *Barium Chloride* may be made from the sulphide of barium obtained by reduction of the sulphate in hydrogen (p. 71). Weigh the sulphide in a crucible, add hydrochloric acid, drop by drop, evaporate, and heat till all odor of acid has disappeared.

3. *Cadmium chloride* may be made from the sulphide obtained by heating cadmium oxide with sulphur (27, p. 70), but the determination is apt to be troublesome, as the salt tends to creep over the edge of the crucible in the final stages of the evaporation.

Lead and silver sulphides are slowly changed into the chlorides by hydrochloric acid, but so many repeated treatments with the acids are necessary to

make the reactions even approximately complete, that these determinations are not recommended.

Use the results of these determinations to find the ratio of chlorine to sulphur, assuming the composition of the sulphide or of the chloride as known.

Example. From 1.192 g. of zinc sulphide was obtained 1.668 g. of zinc chloride. Since the percentage of zinc in zinc chloride is 47.9 % (p. 72), the weight of zinc in both the chloride and sulphide is 0.799 g.; and the ratio of chlorine to sulphur is 869 : 393. Taking the equivalent of chlorine as 35.45, the equivalent of sulphur is found from the ratio above to be 16.03.

32. Halides of the Metals from Other Salts. From their nitrates, the chlorides of lead, potassium, and sodium, and the chloride, bromide, and iodide of silver may be quantitatively made; from carbonates, the chlorides of calcium, lithium, potassium, sodium, and zinc, and fluoride of calcium; from the chlorate and perchlorate, the chloride of potassium. Weigh about one gram of the salt, and proceed as directed in each case.

1. *Nitrates into Chlorides. Lead, potassium,* and *sodium.* Powder and dry the nitrate by heating a little above 100°. Weigh the salt in a porcelain crucible, add a small amount of concentrated hydrochloric acid, and heat (under the hood) with a low flame until the acid has disappeared, and then more strongly, avoiding a red heat. Repeat, if necessary, to constant weight.

The conversion of the potassium nitrate is usually complete the first time; that of the lead and sodium nitrates may require three or four repetitions.

2. *Silver Nitrate into Halides.* Weigh and dissolve the silver nitrate, and convert it into chloride, bromide, or iodide as as in 29, 5, p. 74.

3. *Carbonates into Chlorides. Calcium, lithium, potassium, sodium,* and *zinc.* Proceed as in making the chlorides from oxides (p. 74).

4. *Calcium Carbonate into Fluoride.* Use Iceland spar. Weigh the powdered mineral in a platinum crucible, add hydrofluoric acid, evaporate, and heat till all acid odor has disappeared.

5. *Potassium Chlorate and Perchlorate into Chloride.* Weigh the powdered and dried salt in a crucible or ignition tube, and heat to constant weight.

Conversion of Halides into Other Compounds. The following quantitative reactions may be made. Halides into *nitrates,*—chlorides of barium, lithium, potassium, and sodium ; potassium bromide and iodide (p. 79). Into *sulphates,*—chlorides of barium, calcium, cadmium, potassium, and sodium ; potassium bromide and iodide ; calcium fluoride (p. 87).

XI

THE NITRATES AND DETERMINATION OF NITROGEN IN A NITRATE

Only a few nitrates of the metals can be readily brought into the definite condition demanded for quantitative work. Those which are produced and weighed in the following experiments are: The nitrates of *barium*, *lead*, *lithium*, *potassium*, *silver*, and *sodium*. They are made from the metals, their oxides, or their salts, by the action of nitric acid. The results of the experiments may serve for calculations of the percentage of the metals in the nitrates, and of the equivalent of the nitric acid group.

33. Nitrates from the metals. 1. The *nitrates* of *lead* and *silver* are made as follows: Weigh about one gram of the metal in a porcelain crucible, add some water and then concentrated nitric acid, little by little (*cf.* p. 63), till the metal is all dissolved. Evaporate to dryness on a water bath, and heat over a very low flame till acid vapors cease to appear. Silver nitrate may be heated to fusion without decomposition. Cool and weigh.

2. *Sodium nitrate.* Weigh about 0.5 g. of sodium in a tube (*cf.* p. 61), and proceed as in making sodium chloride from sodium (p. 73), using nitric instead of hydrochloric acid.

Example. In a synthesis of lead nitrate, 1.614 g. of nitrate were produced from 1.008 g. of lead. The

weight of the acid part of the salt is therefore 0.606 g. Percentage composition: lead 62.45 %, acid group 37.55 %. Equivalent of acid group (lead = 103.45):

$$1.008 : 0.606 :: 103.45 : \text{equiv.} = 62.19$$

34. Nitrates from other Compounds. 1. *From Oxides.* *Lead* and *silver oxides* may be changed into nitrates by dissolving in nitric acid and proceeding as in **33**.

2. *Nitrates from Halides.* *Barium*, *lithium*, *potassium*, and *sodium chlorides*, *potassium bromide* and *iodide* can all be converted into nitrates by evaporation with nitric acid. Use either crystallized barium chloride or the anhydrous salt after driving off (and determining) the water of crystallization. The salts should all be pulverized, and dried by heating over a low flame in a porcelain crucible or dish. Avoid melting the salt, but heat it as long as any sound of decrepitation is heard.

Experiments. Weigh about one gram of the salt in a crucible, add a little concentrated nitric acid, and heat (under the hood) over a low flame or on a sand bath till no more acid odor is perceived. Cool and weigh, and repeat the treatment with acid and the heating, till the weight is constant. With barium and potassium chlorides the reaction is usually complete the first time; the others may require two or three repetitions. If there is a tendency to project particles from the crucible during the heating, put a watch-glass on the crucible so as to nearly close it, and heat very carefully. (*Cf.* heating of sulphates, p. 84).

3. *Nitrates from Carbonates.* *Potassium* and *sodium carbonates*, *both acid* and *normal*, and *lithium carbonate*, may be changed into the nitrates. Dry the

normal carbonates by heating, the acid carbonates by pressing between folds of filter paper. Weigh about one gram in a crucible, add dilute nitric acid, drop by drop, till effervescence ceases, evaporate, and heat over a low flame until the acid odor has disappeared.

35. **Reduction of Silver Nitrate to Silver.** When silver nitrate is heated it melts, and then decomposes, leaving a residue of metallic silver. But the result is not quantitative, as some of the substance is carried off by the escaping gases. Silver in silver nitrate may, however, be determined in the following ways:

1. Weigh about 0.5 g. of powdered and dried silver nitrate in a porcelain crucible, and mix it well with several times its bulk of sugar charcoal. Heat with a full Bunsen flame as long as vapors are given off, and then place the crucible on its side on the triangle, and burn off the remaining charcoal. The charcoal burns slowly, and it is best to use the blast lamp. The silver is left as a loose mass of frosted metal.

2. Dissolve the weighed silver nitrate in water, filling the crucible nearly full, and bring into the solution a piece of rather thick sheet copper. Let it stand till a drop of the solution brought in contact with a drop of hydrochloric acid shows no turbidity. Now remove the copper, rubbing off any adhering particles of silver into the crucible, and wash the silver thoroughly with warm water in the crucible, decanting through a small quantitative filter to catch floating particles of metal. Bring the moist filter paper into the crucible, dry over a low flame, and then heat till the paper is burned.

Conversion of Nitrates into Other Compounds. Lead nitrate may be changed to the oxide (p. 68); the

nitrates of lead, potassium, and sodium, to chlorides; the nitrate of silver to chloride, bromide, or iodide (p. 76); and the nitrates of barium, lead, potassium, silver, sodium, and strontium, to sulphates (p. 87).

36. **Determination of the Nitrogen in a Nitrate.** The nitrogen is set free by heating the nitrate with iron, and is collected over water.

Apparatus. A five or six inch test tube, fitted with a rubber stopper and delivery tube; a 200 cc. gas tube.

Experiment. Weigh on a watch-glass about 1.3 g. of sodium nitrate, 1.5 g. of potassium nitrate, or 1.9 g. of barium nitrate (the salts must be powdered and dried). Bring the weighed salt on to a piece of glazed paper and mix it thoroughly with seven or eight times its bulk of iron "reduced by hydrogen." Introduce the mixture into the test tube, and arrange for the collection of the nitrogen. Heat, beginning at the top of the mixture, till no more gas is delivered, then remove the delivery tube from the water and stop heating. Measure the gas with the usual precautions.

Before reducing to normal volume, make a correction for the excess of gas due to the heating, by collecting the air which can be driven off from the same tube with its contents when heated from room temperature to the end temperature of the experiment, and subtracting this volume from the measured volume of the gas.

Calculation. Reduce the corrected volume to normal, find the weight of the nitrogen, and determine the percentage of nitrogen in the nitrate.

37. Composition of Nitrates and of Nitric acid. To solve the first problem, use may be made of the determination of the percentage of sodium in sodium nitrate by a synthesis of the nitrate from the metal (p. 78), and of the percentage of nitrogen found in the last experiment. If we assume that sodium nitrate contains only sodium, nitrogen, and oxygen, the percentage of oxygen is evidently equal to 100 less the sum of the percentages of sodium and nitrogen. From the complete percentage composition of the nitrate, its formula is derived in the usual way.

To find the composition of nitric acid from the composition of sodium nitrate, we need to know the hydrogen equivalent of sodium (p. 61). For if the percentage of sodium in the nitrate is divided by the equivalent of sodium with hydrogen = 1, the quotient, with the percentages of nitrogen and oxygen in the nitrate, will represent the proportions of hydrogen, nitrogen, and oxygen in nitric acid. These figures are readily changed into an expression of the percentage composition of nitric acid; and from either set of values the formula of nitric acid may be derived.

Example. If the sodium in sodium nitrate is found to be 27.00 %, and the nitrogen 16.65 %, the oxygen is $100 - (27.00 + 16.65) = 56.35$ %. Formula of sodium nitrate: $27 \div 23.04 = 1.17$, $16.65 \div 14.04 = 1.18$, and $56.35 \div 16 = 3.52$; the quotients are in the ratio of 1 : 1 : 3 (nearly), hence the formula is $NaNO_3$.

Composition of nitric acid: hydrogen = 27 (percentage of sodium in sodium nitrate) ÷ 23.17 (hydrogen equivalent of sodium found by experiment) = 1.16, nitrogen = 16.65, and oxygen = 56.35. From these figures the percentage composition is found to be,—

hydrogen 1.57 %, nitrogen 22.45 %, and oxygen 75.98 %. The formula: $1.57 \div 1 = 1.57$, $22.45 \div 14.04 = 1.60$, and $75.98 \div 16 = 4.75$; these figures are as 1 : 1 : 3 (nearly), hence the formula is HNO_3.

XII

THE SULPHATES

Many sulphates can be brought into a state suitable for quantitative determinations. Those used in the following experiments are: The sulphates of aluminium, barium, cadmium, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, mercury, nickel, potassium, silver, sodium, strontium, and zinc. They are made from the metals, oxides, sulphides, or salts. The results of the determinations may be used for calculations of the percentages of metals in the sulphates, and of the equivalent of the sulphuric acid group.

The general procedure is this: Weigh the metal or compound in a porcelain crucible, change it into sulphate by sulphuric acid as directed in each case, evaporate on a water bath or over a very low flame (under the hood), and then heat cautiously till all fumes and acid odor have ceased. A few of the sulphates show a tendency to spatter as they approach dryness. It is best in these cases not to try to hasten the experiment by heating too strongly, as the substance is likely to be thrown out of the crucible. If the crucible is inclined so that the substance has more free surface, and the burner is placed so that the heat strikes near the edge of the crucible, the danger of loss from spattering is less. It is also well, if the substance acts badly, to put the crucible in another of the same size for better regulation of the heating. The heating

should, of course, be carried on under a hood. Much time will be saved if a great excess of acid is avoided. Remember that 1 cc. of concentrated sulphuric acid contains about 1.8 g. of H_2SO_4, and make a rough calculation of the amount required. It is better to have to add acid, and heat a second time, than to use an unnecessarily large amount at first. Most of the sulphates withstand a fairly high temperature, but a red heat should be avoided, except with the sulphates of barium, cadmium, magnesium, potassium, and sodium. When the fumes and acid odor have stopped, allow the crucible to cool, and weigh it. It is usually not necessary to heat a second time. If this is done, add two or three drops of concentrated acid before heating.

38. **Sulphates from the Metals.** 1. *By direct action of sulphuric acid. Magnesium* and *zinc.* Weigh about 0.2 g. of magnesium ribbon, or 0.5 g. of pure zinc, dissolve the metal in dilute sulphuric acid (avoid excess) in the crucible, evaporate on a water bath or over a low flame. Heat finally till the bottom of the crucible is a faint red.

Pure zinc dissolves so slowly that it is better to make zinc sulphate through the nitrate, as below.

2. *By sulphuric acid indirectly. a. Calcium* and *sodium.* Weigh about 0.5 g. of the metal (*cf.* pp. 61 and 73 for sodium), treat with water in the crucible, and then add sulphuric acid, drop by drop, till the solution is slightly acid (test with a small bit of litmus paper, leaving it in the solution). Evaporate, and heat to a mild red heat, adding to the sodium salt, at the last, small portions of solid ammonium carbonate to convert the acid sulphate into the normal salt.

b. Cadmium, cobalt, copper, iron, lead, mercury, nickel, lead, silver, and *zinc.* Weigh from 0.5 to 1 g. of the metal, dissolve it in the crucible in nitric acid as directed on page 63, add concentrated sulphuric acid (avoid excess), evaporate, and heat finally to a temperature below red heat, except in the case of cadmium sulphate.

c. Aluminium (zinc). Weigh about 0.2 g. of aluminium, dissolve it in dilute hydrochloric acid, add sulphuric acid (avoid excess of the acids), evaporate, and heat finally to a mild red heat. (Zinc sulphate may also be made through the chloride.)

Example. A synthesis of mercury nitrate gave 2.015 g. of sulphate from 1.366 g. of mercury; the acid group weighs, therefore, 0.649 g. Percentage composition,— mercury 67.79%, acid group 32.21%. Equivalent of acid group (mercury = 100),

$$67.79 : 32.21 :: 100 : \text{equiv.} = 47.51.$$

39. Sulphates from Compounds. 1. *From Oxides. Calcium, chromium, lead, nickel,* and *zinc* sulphates may be made as examples of this transformation. Weigh about 0.5 g. of the oxide, add concentrated sulphuric acid (avoid excess), and heat finally with the precautions described on pages 84 and 85. A little nitric acid should be added in making the lead sulphate. The oxides used may be those obtained as products of other determinations (*cf.* pp. 64, 68 and 69).

2. *From Sulphides. a. Lead.* Weigh about 1 g. of pulverized galena in a crucible, add concentrated nitric acid, and heat over a very low flame till the change is complete, adding a drop or two of sulphuric acid if necessary. *b. Zinc.* Proceed as with zinc oxide.

3. *From Halides.* *Barium, cadmium, calcium, potassium,* and *sodium chlorides; potassium bromide* and *iodide; Calcium fluoride* (*fluorspar*). Proceed as with oxides, except that a platinum crucible must be used for the fluoride. Heat barium sulphate to a mild red heat and the other sulphates as directed on page 85.

Add to the potassium and sodium sulphates, at the last, small portions of ammonium carbonate to change the acid sulphates to the normal salts.

4. *From Nitrates.* *Barium, lead, potassium, silver, sodium* and *strontium.* Proceed as with the oxides. Heat finally as directed on page 85.

5. *From potassium chlorate* and *perchlorate.* Dissolve the salt in water in the crucible, heat on a water bath and add dilute sulphuric acid, drop by drop, till the reaction is finished. Evaporate, and heat with the addition of ammonium carbonate.

6. *From Carbonates.* *Calcium* (*Iceland spar*), *normal* and *acid salts of potassium* and *sodium.* Proceed as with the oxides, heating with ammonium carbonate.

7. *From a Sulphite.* Use *sodium sulphite,* either the crystallized salt, or the anhydrous salt after determining the water of crystallization (p. 92). Proceed as with the carbonates.

40. Reduction of Sulphates. Some sulphates can be reduced quantitatively to the metal, oxide or sulphide. Examples are given in the following paragraphs:

1. *Reduction to Metal.* *Copper* and *silver* sulphates are reduced to the metals by heating in hydrogen. Either the crystallized or the anhydrous salt of

copper may be used. Proceed exactly as in the reduction of the oxides (p. 66).

2. *Reduction to Oxide.* *Copper*, *manganese*, and *ferrous-ammonium* sulphates are changed to oxides by heating. Weigh the sulphates in a crucible, mix thoroughly with ammonium carbonate, and heat strongly with full Bunsen flame or the blast lamp. (*Cf.* p. 68.)

3. *Reduction to sulphide.* *Barium* sulphate is reduced to sulphide by heating in hydrogen as in the case of the oxides (p. 66). *Lead* and *zinc* sulphates are changed to sulphides by mixing them with sulphur and heating in a crucible (*cf.* p. 71). It is usually necessary to repeat the treatment with sulphur and the heating three or four times to make the reaction complete.

41. The Composition of Sulphates and of Sulphuric Acid. A method for finding the composition of sulphates and sulphuric acid may be based on determinations of the percentage of zinc in zinc sulphate by a synthesis of this compound from the metal (p. 85); of the amount of zinc sulphide obtained from the sulphate (40, 3); and of the hydrogen equivalent of zinc (p. 60). The calculation is similar to that described for finding the composition of nitrates and nitric acid (p. 82).

XIII

THE COMPOSITION OF CARBONATES

Most of the carbonates lose carbon dioxide when heated, and all lose it when treated with hydrochloric acid; some of them yield carbon monoxide when heated with zinc dust. These reactions may be employed in the case of a few normal carbonates as aids in determining the composition of these salts and of carbonic acid.

42. Determination of Carbon Dioxide by Heat. Calcium carbonate (best in the form of Iceland spar), magnesium carbonate in the form of magnesite, and zinc carbonate, may be used. Weigh about one gram of the finely powdered and dried carbonate in a porcelain crucible, and heat it strongly for 20 minutes. After cooling and weighing, heat again for 5 to 10 minutes, at a time, to constant weight. Calcium carbonate requires a higher temperature than the others, and is best heated by the blast lamp. Weigh the calcium oxide as soon as the crucible is cool, or keep in a desiccator until weighed. Calculate the percentage of carbon dioxide in the carbonate.

43. Determination of Carbon Dioxide by Hydrochloric Acid. Use the same carbonates as in 42, or manganese carbonate which has been dried in a desiccator.

Apparatus. A 60 cc. conical flask, fitted with a stopper and a small straight calcium chloride tube.

Experiment. Put into the flask about 30 cc. of dilute hydrochloric acid (1 : 6), and add about 0.5 g. of powdered marble to saturate the acid with carbon dioxide. While the marble is dissolving, weigh about one gram of the carbonate. When the marble is all dissolved, aspirate the carbon dioxide from above the liquid, and weigh the flask with the stopper and drying tube. Now drop into the flask the weighed carbonate and insert the stopper. When the carbonate has disappeared, aspirate the carbon dioxide from the flask and from the drying tube, being careful not to remove any of the water which may be on the neck of the flask and the stopper, and weigh them.

This method can be used to determine the carbon dioxide from any carbonate, normal, acid, or basic.

44. Analysis of a Carbonate by Hydrogen. Manganese carbonate is converted into the monoxide by heating in hydrogen. The carbonate should be dried over sulphuric acid, and the experiment carried out as in the reduction of the oxides by hydrogen (p. 66). When manganese carbonate is heated in air till uniformly brown, it is changed into Mn_3O_4.

45. Determination of Carbon Monoxide from a Carbonate. Weigh not more than 780 mg. (for a 200 cc. gas tube) of finely powdered Iceland spar, or dried "precipitated chalk," and proceed as in the determination of nitrogen in a nitrate (p. 81), but use zinc dust instead of iron, and an ignition tube of hard glass instead of a test tube. The gas comes off slowly toward the last, and it is well to heat finally with two burners. Correct for the gas driven over by expan-

sion as in the nitrogen determination. Find the normal volume and weight of the carbon monoxide, and its percentage in the carbonate.

46. Composition of Carbonates and of Carbonic Acid. From the data obtained in the foregoing experiments, in the synthesis of the corresponding metallic oxide (*cf.* p. 63), and in density determinations of carbon dioxide and monoxide (*cf.* p. 36), the composition and formulas of normal carbonates and carbonic acid may be derived. The method of calculation is like that employed in the case of the nitrates and sulphates (*cf.* pp. 82 and 88.)

Conversion of Carbonates into Other Salts. Into halides (p. 77); into nitrates (p. 79); into sulphates (p. 87).

XIV

VARIOUS QUANTITATIVE EXERCISES

47. Determination of the Water of Crystallization. 1. The water of crystallization of a number of salts is readily determined by heating the crystallized salt in a crucible to a temperature below that at which the anhydrous salt decomposes. *Barium chloride*, *calcium sulphate* (*gypsum*), and *magnesium sulphate* are heated so that the bottom of the crucible is faintly red; with *copper sulphate*, *manganese sulphate*, and *sodium sulphite*, the flame should be of half height and not touch the crucible; *ammonium alum* should be heated by a flame about two inches high with its top two inches below the crucible. In the last four cases it is well to place the crucible in another of the same size to avoid over-heating.

2. Another way of carrying out the experiment is to weigh the salt in a test tube, and connect the test tube with a Chapman aspirator. Under the reduced pressure the water is given off at a lower temperature with less danger of decomposing the salt. The only difficulty is that particles of the salt may possibly be carried out of the tube in the current of vapor.

Ammonium alum, magnesium sulphate, and sodium sulphite, melt in their water of crystallization. All the salts should be powdered, and dried by pressing between folds of filter paper before weighing.

Find the percentage of the water of crystallization and calculate the number of molecules of water in the crystallized salt.

Example. 1.439 g. of crystallized manganese sulphate lost 0.465 g. of water; anhydrous sulphate = 0.974 g. Percentage of water = 32.31. Molecules of water:

$$974 : 465 :: \text{mol. wt. } MnSO_4 : 18x$$
$$151.06 : 18x$$

whence $18x = 72.2$, and $x = 4$ (very nearly).

48. Analysis of Ammonium Dichromate. Determine the chromium oxide by heating in a crucible as described on p. 69. To determine the nitrogen: weigh not more than two grams of the salt on a watch-glass, mix it on glazed paper with 7 or 8 times its bulk of clean, dry sand, and introduce the mixture into a 7 inch test tube, fitted with a stopper and delivery tube. Arrange a 200 cc. gas tube for collecting the nitrogen over water, and heat the mixture in the test tube, beginning at the top. Correct for the expansion by heat by subtracting from the uncorrected volume of gas the volume of air which can be driven from a test tube of the same size, filled to the same height with sand alone, when heated to the same temperature. Find the normal volume and the weight of the nitrogen.

The determinations give the proportions of chromium oxide, of nitrogen, and, by loss, of water, which can be obtained from the dichromate. Assuming the composition of the oxide and water as known, find the percentage of each of the elements, and the formula of the salt.

49. Synthesis of a Sulphate from the Metal and Sulphur Dioxide. 1. To make a solution of sulphuric acid containing a known weight of sulphur dioxide in each cubic centimeter: Fill a 500 cc. round-

bottomed flask with sulphur dioxide and determine its weight as in the density experiments (p. 36). Measure 100 cc. of hydrogen peroxide solution, and open the short tube of the flask under its surface; allow most of it to enter the flask, and rinse it about in the flask to dissolve and oxidize the dioxide. Now pour the solution in the flask into a 200 cc. graduated cylinder, add the rest of the peroxide solution, and fill up exactly to the 200 cc. mark with water which is used to rinse out the flask.

2. To make a solution of sodium hydroxide containing a known weight of sodium in each cubic centimeter: Weigh about 1 g. of sodium in a tube (*cf.* p. 61), bring it into about 150 cc. of water in a dish, and when it has all dissolved, make the solution up to exactly 200 cc. with water used to rinse the dish.

3. Now fill two burettes with the solutions, and find the volumes which exactly neutralize each other, using litmus or phenolphthalein as an indicator.

Calculation. From the results calculate the ratio of sodium to sulphur dioxide in the sulphate. By determining, further, the ratio of sodium to the sulphuric acid group by making sodium sulphate from the metal and the acid (p. 85); and the ratio of sulphur to sulphur dioxide by a synthesis of the dioxide (p. 54), the composition of the sulphate in detail may be found.

As the solution of hydrogen peroxide often contains acid, a correction should be made for this if it is present. Since 100 cc. of the peroxide solution were used in making the 200 cc. of sulphuric acid solution, each cubic centimeter of the latter contains 0.5 cc. of the former. Titrate a sample of the peroxide solution with the sodium hydroxide solution, calculate how

much of the latter would be necessary to neutralize the acid from the peroxide in each measured volume of the sulphuric acid solution used in titration, and subtract this from the corresponding volumes of the sodium hydroxide solution.

50. **Sodium Chloride from Sodium and Hydrogen Chloride.** Fill a round-bottomed flask with hydrogen chloride and determine the weight of the gas (p. 35). Dissolve the gas in a little water (*cf.* p. 48) and make the solution up to a measured volume. Make a solution of sodium hydroxide from a weighed amount of sodium as in 49, 2. Titrate the solutions against each other. Find the ratio of sodium to hydrogen chloride from the results. Using the data from an analysis of hydrogen chloride (p. 46), determine the ratio of sodium to chlorine.

51. **Analysis of Hydrogen and of Sodium Peroxides.** *Apparatus.* A 100 cc. conical flask, fitted with a stopper carrying a separatory funnel, or its substitute (*cf.* Appendix), and a delivery tube; a 200 cc. gas tube.

Experiment. Make a solution of potassium permanganate, dissolving about 10 g. in 100 cc. of water. Measure in a small graduated cylinder 10 to 15 cc. of the peroxide solution (less if the solution is a strong one), bring it into the flask, and add about 4 cc. of dilute sulphuric acid (1 : 5). Measure 20 cc. of the permanganate solution, put it in the funnel and let it run down to fill the stem; then insert the stopper and arrange for the collection of the oxygen over water. Now let the permanganate drop slowly into the flask. When it is all brought into the flask, the contents should be deeply colored. Read the volume of gas in

the usual manner, and subtract from its volume that of the permanganate solution which was used. Then calculate the normal volume and the weight of the oxygen. Only one-half of the oxygen comes from the peroxide. Calculate its percentage by volume and by weight.

Sodium peroxide may be analyzed in a similar manner. Weigh a little more than 1 g. of the peroxide and bring it into the dry flask. Standing the flask in a dish of water, measure into the funnel 20 cc. of water, letting it run down to fill the stem, and proceed as in the analysis of hydrogen peroxide. In this case all of the oxygen comes from the peroxide.

52. **Analysis of a Silver Coin.** 1. Weigh in a crucible about one gram of the alloy cut from a ten cent piece, and dissolve it in dilute nitric acid (avoid excess) on a water bath. Put in the solution a short strip of rather thick sheet copper, and leave it until a drop of the solution shows no turbidity with a drop of dilute hydrochloric acid. Then remove the copper, rubbing off any adherent silver with a glass rod. Pour off the solution (down a glass rod) on to a quantitative filter, and wash thoroughly, decanting on to the filter. Bring the filter into the crucible, dry it over a low flame, and then heat till it is completely burned.

Calculate the percentage of silver in the coin.

2. Weigh and dissolve the alloy as in 1. Add about 5 cc. of dilute sulphuric acid (1 : 4), evaporate on the water bath, and then heat over a low flame till no more acid fumes or odor are perceived. In the heating, place the crucible in another of the same size and let the flame barely touch the outer crucible. Towards

the end, add small portions of solid ammonium carbonate. If no sulphuric acid fumes appear when the substance is heated, cool the crucible, add a few drops of concentrated acid, and heat again. Cool and weigh. Heat again, if necessary, with addition of a drop or two of acid, until the weight is constant.

Calculation. The calculated ratio of silver to silver sulphate is 1 : 1.445, and that of copper to copper sulphate is 1 : 2.51; if we let a = weight of the coin taken, b = the weight of the sulphates, and x = the weight of the silver;

$$1.445x + 2.51\,(a - x) = b,$$

$$\text{and } x = \frac{2.51a - b}{1.065}.$$

Example. Weight of coin was 708 mg., of sulphates was 1095 mg. $x = \dfrac{(251 \times 708) - 1095}{1.065} = 640.4$; hence the percentage of silver in the coin is 90.45 %.

53. **Determination of Copper in Brass.** Weigh in a crucible about one gram of brass, and dissolve it in nitric acid as in the case of the coin. Add to the solution a little dilute sulphuric acid and a piece of zinc about equal in weight to the brass. If the color of the solution has not all disappeared some time before the zinc is dissolved, add very small pieces from time to time till the color is completely gone. Let the crucible stand till it is certain that all of the zinc is dissolved, adding a little sulphuric acid if necessary. Pour off the solution (down a glass rod), and wash thoroughly by decantation, using alcohol for the final washing. Dry on a water bath.

Calculate the percentage of copper in brass.

APPENDIX

I

SUGGESTIONS FOR THE EXPERIMENTAL WORK

1. Determinations in Series. A number of successive determinations may be made from the same amount of original substance, the weighed product of one reaction being used as the starting point for another determination. Some of these serial determinations are given below. One or more of the steps may be omitted in many cases, and series may be begun at any point.

1. $BaCl_2,2H_2O - BaCl_2 - Ba2NO_3 - BaSO_4$.
2. $Cd - CdO - CdCl_2 - CdSO_4$.
3. $Ca - Ca(OH)_2 - CaO - CaCl_2 - CaSO_4$.
4. $CaCO_3 - CaO - Ca(OH)_2 - CaCl_2 - CaSO_4$.
5. $CuSO_4, 5H_2O - CuSO_4 - CuO$.
6. $Fe - Fe_2O_3 - Fe_23SO_4$
7. $Pb - PbO - PbCl_2$ or $Pb2NO_3 - PbSO_4$.
8. $Mg - MgO - MgSO_4$.
9. $MnSO_4,4H_2O - MnSO_4 - Mn_3O_4$.
10. $Ni - NiO - NiSO_4$.
11. $KClO_4$ or $KClO_3 - KCl - KNO_3 - K_2SO_4$.
12. $KHCO_3$ or $K_2CO_3 - KCl$ or $KNO_3 - K_2SO_4$.
13. KBr or $KI - KNO_3 - K_2SO_4$.
14. $Ag_2O - AgNO_3 - Ag_2SO_4$.
15. $Na - NaCl$ or $NaNO_3 - NaNO_3$ or $NaCl - Na_2SO_4$.
16. $Zn - ZnO - ZnSO_4$.

2. Illustrations of the Law of Multiple Proportions.

1. Reduction of the higher oxides of lead into the monoxide, and of this into lead.
2. Reduction of cupric and of cuprous oxides into copper.
3. Reduction of manganese dioxide to mangano-manganic oxide, and of the latter to manganese monoxide.

4. Conversion of sodium chloride into sodium sulphate, and of sodium sulphite into sodium chloride.

5. Conversion of potassium perchlorate and chlorate into potassium chloride.

6. Preparation of cuprous sulphide from copper and from cupric sulphide.

7. Preparation of ferrous sulphide from iron and from iron disulphide (pyrites).

8. Reduction of stannic sulphide to stannous sulphide.

9. Reduction of carbon dioxide to carbon monoxide.

In the last two cases the second transformation is not made, but the presence of sulphur or oxygen in the lower compound may be easily proved, and this shows that there are two compounds of tin and of carbon which contain the same elements in *different* proportions; that the proportions are *multiple* requires further evidence.

3. Changes which may be Made in Either Direction. In a number of instances the product of a reaction may be changed back into the original substance, *e. g.* silver nitrate may be quantitatively made from silver, and quantitatively reduced to silver. In the following list several such reversible determinations are indicated:

$Bi - Bi_2O_3$	$Hg - HgO$
$Cd - CdO$	$Ni - NiO$
$CaO - Ca(OH)_2$	$KCl - KNO_3$
$Co - Co_3O_4$	$Ag - AgNO_3$
$Cu - CuO$	$Ag - Ag_2S$
$CuO - CuSO_4$	$Ag - Ag_2SO_4$
$Fe - Fe_2O_3$	$NaCl - NaNO_3$
$Pb - PbO$	$ZnS - ZnSO_4$
$MnO - Mn_3O_4$	

II

APPARATUS

The Balance should be sensitive to about one milligram. A more sensitive balance is unnecessary, and is inadvisable because the weighings would take a longer time than is justified by the

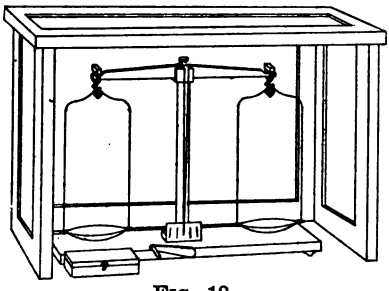

FIG. 18.

probable accuracy of the manipulation. Becker's No. 30 is a good balance for the work. It can be imported, duty free, on a plain board base without the drawer, for about $5.50. The balance must be protected from currents of air during the weighings. A screen for this purpose is represented in Fig. 18. The frame is 20 cm. wider and 10 cm. deeper than the base of the balance, and the back, sides and top, are closed by glass (or white cloth). A piece of heavy cloth (not shown in cut) tacked to the upper front edge closes the front, and is thrown back on the top when the balance is in use.

Weights. A set of weights from 50 grams to 1 mg. can be imported duty free for about $1.50.

Barometer. The siphon barometer is a good and inexpensive one for chemical use. The scale is usually etched on the glass, and readings are made at both of the mercury levels and either added or subtracted, according to the construction of the scale. The barometer should be tapped lightly or swung a little from side to side before reading it, to make the meniscus heights equal, but must hang vertically when the readings are made.

Thermometers. The zero point and the boiling point of the thermometer should be determined, and the scale readings corrected from these data. To determine the zero point, fill a large funnel with crushed ice, and put the thermometer in the ice, sinking it to the zero mark. When the mercury is stationary, read the true zero point. To find the boiling point, suspend the thermometer in steam from boiling water in a long necked flask or a cylinder. The cork which holds the thermometer is cut in several places on its side so that the steam may escape freely. The thermometer must not touch the water, and the mercury at its highest point should be barely above the cork. Read the position of the mercury when it becomes stationary, and also the barometer. Correct the boiling point by multiplying 0.0375° by the difference between the corrected barometer read-

ing and 760 mm., and adding the product to the observed boiling point if the barometer is below 760 mm., or subtracting, if it is above. It is not necessary for these experiments to calibrate the thermometer.

The Reaction Tubes used in a number of the experiments are made from combustion tubing, having an inside diameter of from 8 to 10 mm., and walls of medium thickness. They are usually from 18 to 20 cm. long, and though they may be left of the same diameter at each end, it is better in most cases to draw one end out as shown in Fig. 19.

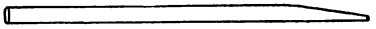

FIG. 19.

Ignition Tubes (Figs. 6 and 7, pp. 28, 30), are made of the same tubing used for the reaction tubes.

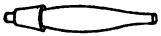

FIG. 20.

Adapters (Fig. 20) are made of soft glass tubing, about 8 mm. in outside diameter. A section of rubber tubing is slipped over the end, forming an adjustable stopper.

Dropping Funnel. In place of the glass stoppered separatory funnel one of the following substitutes may be used:

1. A glass rod about 10 cm. long, and of a size to just slip into the throat of an ordinary funnel, is drawn out to a conical end, and a short piece of tightly fitting black rubber tubing is pushed on to this end. This makes a valve by which the flow of liquid through the funnel may be controlled.

2. The apparatus is represented in Fig. 21. Before inserting the stopper in the reaction flask (the lower one in the cut), the siphon is filled with the liquid in the upper flask by blowing into the rubber tube, and then closing the latter by the screw pinchcock. This arrangement is suited to those cases where the liquid would act on rubber.

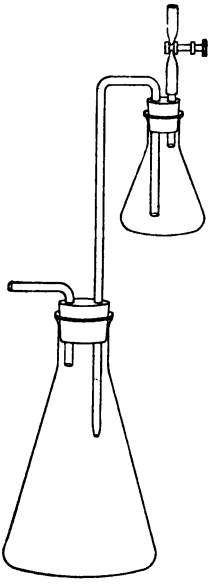

FIG. 21.

An Aspirator is necessary in several experiments to draw air or other gases through the apparatus. A water filter pump, such as Chapman's, is the most serviceable, but, in place of this, a siphon aspirator like that shown in Fig. 22 may be used. In either case the stream of gas is regulated by a screw pinch-cock.

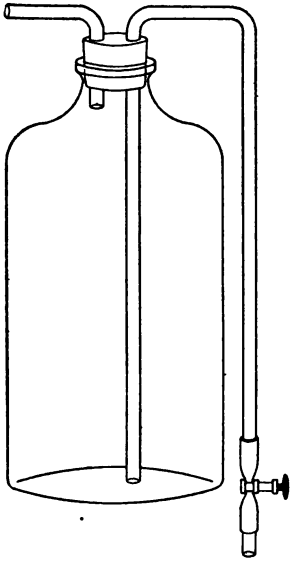

FIG. 22.

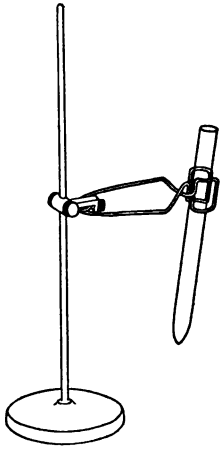

FIG. 23.

The Small Stand with Spring Clamp (Fig. 23) will be found convenient for supporting tubes and other apparatus. It is manufactured by the Central Scientific Co. of Chicago.

Chimney Tripods are very useful for supporting crucibles on triangles in the many cases where substances must be heated carefully with a low flame. The chimney is a cylinder of sheet iron, about 2½ inches in diameter, and 5 or 6 inches long, on tripod legs. Its lower edge should be an inch or so below the top of the burner, with a vertical slot cut in it to allow the burner to be slipped under it, or removed readily. If these tripods are not available, burner chimneys should be used with low flames to insure steady heating.

Grease for sealing connections between rubber and glass, or between glass and glass, as in a desiccator, is made by melting beeswax and vaseline together in the proportion of about one to four, so that the mixture when cold has the consistency of butter.

A Rubber Pad for closing gas tubes, when a gas must be collected over a solution of caustic alkali, is made from a section of a large rubber stopper. One end of a stout iron wire is made into a flat coil and the wire bent at a right angle close to the coil to form a handle. The pad is placed on the coil and fastened to it by fine wire threaded through the edge of the rubber.

Other Apparatus:

Graduated Cylinders, 250, 100, 50, 25 and 10 cc.
Graduated Gas Tubes, 200 or 100 cc.
Round Bottom Flasks, 500 and 300 cc.
Conical Flasks, 350, 200, 150, 100 and 60 cc.
Porcelain Crucibles, 50 cc.
Platinum Crucible (two experiments).
Watch Glasses, 4 or 5 cm. in diameter.
Wash Bottles and Drying Tubes.
Potash Bulbs (one experiment).
Burettes (two experiments).
Gas Generators.
Deep Glass Cylinder for adjusting gas volumes.
Glazed Paper and Camel's Hair Brush.
Water and Sand Baths, Crucible Tongs, Pipe-stem Triangles, Screw Pinch-cocks, Burners, Glass and Rubber Tubing, etc.

CHEMICALS

Substances used for the determinations. Those which may be the product of previous determinations are printed in italics.

Alum, Ammonium
Aluminium
Ammonium Dichromate
Antimony
Arsenic Trioxide
Barium Chloride
Chloride cryst.
Barium Nitrate
Sulphate
Bismuth
Oxide
Cadmium
Chloride
Oxide

[1]Calcium
Carbonate
Hydroxide
Oxide
Chromium Oxide, Cr_2O_3
Cobalt
Oxide, Co_3O_4
Copper
Oxide, *CuO*
[2]Oxide, Cu_2O
Sulphate
Sulphate, cryst.
[3]Sulphide CuS
Iron "reduced by hydrogen"
[4]Wire
Oxide, Fe_2O_3
Ferrous-Ammonium Sulphate
Lead
Dioxide, PbO_2
Monoxide, *PbO*
Sesquioxide, Pb_2O_3
"Red Lead," Pb_3O_4
Nitrate
Sulphate
Lithium Chloride
Carbonate
Magnesium, ribbon
Magnesium Oxide
Sulphate
Sulphate, cryst.
Manganese Dioxide, MnO_2
Mangano-manganic Oxide, M_3O_4
Manganous Oxide, *MnO*
Carbonate
Sulphate
Sulphate, cryst.
Mercury
Oxide, *HgO*
Nickel
Oxide, *NiO*
Potassium Bromide
Carbonate
Hydrogen Carbonate
Chlorate
Chloride
Nitrate
Perchlorate
Silver
[5]Oxide
Nitrate
Sulphate
Sodium
Borate (borax), cryst.
Carbonate

1 The metal calcium can now be obtained in a fair state of purity and at a moderate price. It is too hard to be cut easily with a knife, but is readily cut by a fine saw. The pieces should be brightened with a file or knife just before they are used. The action on water becomes slow and almost stops unless the amount of water is large.

2 Pure cuprous oxide (Kahlbaum's) must be kept sealed in small bottles till used.

3 Cupric sulphide is prepared in the laboratory by precipitating a solution of copper sulphate with hydrogen sulphide. Filter rapidly with a filter pump, wash thoroughly with water containing hydrogen sulphide, press out most of the water between folds of filter paper, dry on a water bath or radiator, and finally, over sulphuric acid.

4 The iron wire should be the fine wire used for standardizing in volumetric work.

5 The preparation of silver oxide has been described on page 65.

Sodium Hydrogen Carbonate
Chloride
Nitrate
Sulphite
Sulphite, cryst.
Strontium Nitrate
Tin
Oxide, SnO_2
Sulphide, SnS_2
Zinc
Chloride
Zinc Oxide
Sulphate
Sulphide

Minerals

Calcite, Iceland spar
Fluor spar
Galena
Gypsum
Pyrites

PREPARATION OF GASES FOR THE EXPERIMENTS

Gases from the generators must usually be purified and dried. It is ordinarily sufficient to pass the gas through a wash bottle containing water, and then through concentrated sulphuric acid, or through a tube filled with granulated calcium chloride. Instead of a sulphuric acid wash bottle, a U tube, filled with glass beads moistened with the acid, may be employed to advantage. In the density experiments it is important that the gas be cool when it enters the density flask. In those cases, therefore, in which the gas for such determinations is produced by heating, a water wash bottle and drying tube should be used, even if the gas does not need purification.

As it is often convenient to know how much substance to take for the preparation of a gas, the weight required to produce one liter (normal) is given with the directions for making the gases.

The dilution of acids is indicated by ratios which express the volumes of concentrated acid and of water.

Acetylene. By dropping water on to calcium carbide. One liter is made from about 3 grams of carbide.

Ammonia. 1. By heating a concentrated solution of ammonia. 2. By dropping concentrated ammonia on to solid sodium or potassium hydroxide.

Ammonia is dried by passing it through a U tube filled with fragments of fused potassium hydroxide, or with quick-lime, or soda-lime.

Carbon Dioxide. 1. By the action of hydrochloric acid on marble. Fragments of marble are covered with water, and concentrated hydrochloric acid added from time to time. One liter of the gas is obtained from 4.5 grams of marble.

2. By dropping hydrochloric acid (1 : 1), or sulphuric acid (1 : 4), on to acid sodium carbonate. One liter is obtained from about 3.8 grams of the carbonate.

Carbon Monoxide. By passing carbon dioxide through a tube containing heated zinc dust. The gas is washed by a solution of caustic soda, and dried by soda-lime. One liter should be obtained from about 10 grams of zinc dust.

Chlorine. 1. By gently heating manganese dioxide with concentrated hydrochloric acid. The dioxide should be in lumps. One liter of chlorine should be obtained from 5 grams of the dioxide.

2. By heating a mixture of equal parts of common salt and manganese dioxide with sulphuric acid (1 : 1). One liter is obtained from about 5.3 grams of salt.

Chlorine is dried with sulphuric acid.

Hydrogen. By the action of dilute sulphuric acid (1 : 10), or hydrochloric acid (1 : 5), on granulated zinc. (Zinc is granulated by melting the sticks in the flame of the blast lamp, and allowing the molten drops to fall into water from a height of five or six feet.) The action of the acid on pure zinc is very slow, but can be rendered more rapid by adding a few drops of copper sulphate solution. If the generator is a small one, it should be placed in water to prevent undue heating. One liter of hydrogen requires about 3 grams of zinc.

Hydrogen Chloride. 1. By gently heating concentrated hydrochloric acid.

2. By dropping concentrated sulphuric acid on to concentrated hydrochloric acid.

3. By dropping concentrated sulphuric acid on to common salt. One liter of the gas is obtained from about 2.6 grams of salt.

Hydrogen Sulphide. By heating antimony sulphide (stibnite) with concentrated hydrochloric acid. One liter requires about 5 grams of the sulphide.

Nitrogen. "*Atmospheric nitrogen*" is prepared by passing air through a tube containing heated copper. It is purified and dried by a tube filled with solid potassium hydroxide or soda-lime.

"*Chemical nitrogen*" may be prepared by heating ammonium dichromate, powdered and mixed with about 8 times its bulk of clean sand. One liter of nitrogen is obtained from about 11.3 grams of the dichromate.

Nitric Oxide. 1. From the action of nitric acid (1:1) on copper clippings. The action of the acid is controlled by adding water or concentrated acid.

2. By dropping concentrated sulphuric acid on to a mixture of copper clippings and potassium or sodium nitrate.

Nitrous Oxide. By heating ammonium nitrate. This requires care, as the melted salt is liable to froth and the evolution of gas to become too rapid. A wide delivery tube should be used, and the heating conducted cautiously with a low flame. One liter of the gas is obtained from about 3.6 grams of the nitrate.

Oxygen. 1. By heating a mixture of equal parts of potassium chlorate and manganese dioxide. The gas should be washed with a dilute solution of caustic soda. One liter of oxygen requires about 3.65 grams of the chlorate.

2. A purer gas is obtained by dropping water on to sodium peroxide. One liter requires 6 or 7 grams of peroxide.

3. Another good method is by heating potassium permanganate with sulphuric acid (1:4) in the proportion of 1 gram of permanganate to 4 or 5 cc. of acid. The oxygen begins to come off at 50° and its evolution is readily controlled. (Riggs in *Jour. Am. Chem. Soc.*, Vol. 25, p. 876.) One liter of oxygen is obtained from about 10 grams of the permanganate.

Sulphur Dioxide. By heating copper clippings with concentrated sulphuric acid. One liter should be obtained from about 3 grams of copper.

2. By dropping sulphuric acid (1:1) on to acid sodium sulphite. One liter of sulphur dioxide requires 4.75 grams of the sulphite.

ATOMIC WEIGHTS AND EQUIVALENTS

	Atomic Weights	Equivalents		Atomic Weights	Equivalents
Aluminium	27.1	9.03	Iron	55.9	27.95
Antimony	120.2	40.07	Lead	206.9	103.45
Arsenic	75	25	Lithium	7.03	7.03
Barium	137.4	68.7	Magnesium	24.36	12.18
Bismuth	208.5	69.5	Manganese	55	27.5
Boron	11	3.67	Mercury	200	100
Bromine	79.96	79.96	Nickel	58.7	29.35
Cadmium	112.4	56.2	Nitrogen	14.04	14.04
Calcium	40.1	20.05	Oxygen	16	16
Carbon	12	12	Potassium	39.15	39.15
Chlorine	35.45	35.45	Silicon	28.4	7.1
Chromium	52.1	17.37	Silver	107.93	107.93
Cobalt	59	29.5	Sodium	23.05	23.05
Copper	63.6	63.6	Strontium	87.6	43.8
Fluorine	19	19	Sulphur	32.06	16.03
Hydrogen	1.008	1.008	Tin	119	59.5
Iodine	126.97	126.97	Zinc	65.4	32.7

SPECIFIC HEATS OF METALS

	Specific Heats	Atomic Heats		Specific Heats	Atomic Heats
Aluminium	.222	6.01	Magnesium	.245	5.97
Antimony	.495	5.95	Mercury	.033	6.60
Bismuth	.308	6.42	Nickel	.109	6.40
Cadmium	.057	6.41	Platinum	.032	6.23
Copper	.093	5.91	Silver	.056	6.04
Iron	.114	6.37	Tin	.056	6.66
Lead	.031	6.40	Zinc	.096	6.28

THE DENSITIES OF GASES, AND THE WEIGHT OF 1 CC. under standard conditions of temperature and pressure, and at latitude 41° at sea level

Formulas	Densities (Air = 1) Observed Values	Densities (Air = 1) Theoretical Values	Weights of 1 cc. in mg. Observed Values	Weights of 1 cc. in mg. Theoretical Values	Molecular Weights
Air	1.0000		1.2923		
C_2H_2	0.92	0.8988	1.1889	1.1615	26.02
NH_3	0.5971	0.5895	0.7716	0.7618	17.06
CO_2	1.5291	1.5201	1.9761	1.9645	44.00
CO	0.9672	0.9673	1.2499	1.2501	28.00
Cl_2	2.491	2.4494	3.2192	3.1654	70.90
H_2	0.06926	0.06965	0.0895	0.0900	2.016
HCl	1.2692	1.2595	1.6402	1.6276	36.46
H_2S	1.1895	1.1773	1.5372	1.5215	34.08
NO	1.0372	1.0378	1.3404	1.3412	30.04
N_2	0.9672	0.9701	1.2499	1.2537	28.08
N_2O	1.5301	1.5229	1.9774	1.9681	44.08
O_2	1.10535	1.1055	1.4285	1.4287	32.00
SO_2	2.2639	2.2131	2.9257	2.8600	64.06

The densities are taken from Landolt and Börnstein's "*Tabellen*"; the "observed" and "theoretical" weights of 1 cc. at latitude 41° are calculated from these densities.

The standard barometric height (760 mm.) represents different pressures at different latitudes and at different altitudes, because of changes in the value of gravity; and since the weight of gas in 1 cc. varies with the pressure, an exact statement of this weight can be made only with reference to a definite latitude and altitude. The usual altitude chosen as standard is the sea level, and the latitude in most tables is 45°. Latitude 41° is selected as a suitable parallel for the United States (*cf.* Wells' "*Chemical Calculations*").

The corrections for latitude and altitude are in most instances too small to be of importance in ordinary work with gases,—that for latitude is about $\frac{1}{111}$th for each degree between 35° and 50°, to be added or subtracted as the latitude is higher or lower; and that for altitude is made by subtracting $\frac{1}{1000}$th for each thousand feet above the sea level.

TENSION OF AQUEOUS VAPOR IN MILLEMETERS OF MERCURY

°C	Tension	°C	Tension	°C	Tension	°C	Tension
0.0	4.6	14.0	11.9	18.5	15.8	23.0	20.9
10.0	9.2	14.5	12.3	19.0	16.3	23.5	21.5
10.5	9.5	15.0	12.7	19.5	16.9	24.0	22.2
11.0	9.8	15.5	13.1	20.0	17.4	24.5	22.9
11.5	10.1	16.0	13.5	20.5	17.9	25.0	23.6
12.0	10.5	16.5	14.0	21.0	18.5	25.5	24.3
12.5	10.8	17.0	14.4	21.5	19.1	26.0	25.0
13.0	11.2	17.5	14.9	22.0	19.7	26.5	25.7
13.5	11.5	18.0	15.4	22.5	20.3	27.0	26.5

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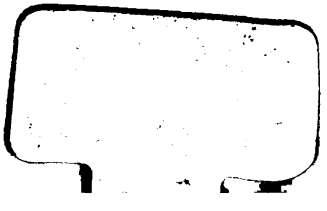
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